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Atomic Molecular Theory

Introduction

In this study, our goal is to develop the concept of the Atomic Molecular Theory. This is the theory at the foundation of everything we understand about Chemistry, as it states that all matter is made up of individual particles called atoms, which combine in ways that are both simple and complex to form larger particles called molecules. When we understand these atoms and molecules, it changes the way that we look at the world around us. We can understand the properties of the substances we interact with, we can make predictions about the changes and reactions that these substances will undergo, and we can design materials with properties that would be useful to us.

The idea that everything is made of atoms is something we are told at a very early age, and for many students, it is hard then to imagine a world in which we don't know that everything is made of atoms. On the other hand, this "particulate view" of matter does seem counter to almost all of our own observations. The desks in front of us, the air we breathe, the water we drink, and even our own flesh show no signs of these particles. Quite the opposite: they seem to be either very solid or quite fluid, and certainly not grainy like a collection of particles might be expected to be.

In this concept development study, then, we set aside our knowledge of these atoms and molecules and ask, quite skeptically, why do we believe that there are atoms that combine to form molecules? Or asked another way, if we believe that all matter is made up of atoms, how would we show that this is true? What is the evidence? Does the proof require us to "see" atoms, or is it possible to prove that they exist without actually seeing them?

Foundation

Chemistry is the study of matter, so it makes sense for us to agree on what we mean by matter and what we want to know about it. Technically, matter is anything that has mass, but more commonly, matter is what we regard as "stuff." Anything that has physical properties and takes up space, whether a

solid, a liquid, or gas, is matter. Matter can be anything from microscopic to galactic, or from rocks and air to butterflies and humans. But we can go further than this and focus on a specific type of matter called a pure substance. This is a material that is completely uniform in properties regardless of the size of the sample we take or from where we take the sample. It is easiest to understand a pure substance by comparing it to a mixture, which may or may not be uniform in its properties such as color, density, and texture and can vary depending on how we make the mixture or its origin. Showing that a substance is either a pure substance or a mixture requires a lot of experimentation, but we will assume for our foundation that we have already identified which samples of matter are pure substances and which are mixtures.

As of 2013, the most comprehensive list of chemical substances numbered over 70 million entries. This huge number of materials seems incomprehensible, far beyond our understanding. However, it turns out that these 70 million substances are all made up from a much smaller set of pure substances called elements. An element is a substance, which cannot be broken down into simpler substances. There are only about 90 commonly occurring elements on earth. The remaining 70 million pure substances are combinations of these elements called compounds, and these are distinguishable from the elements in that a compound can be broken down into the elements from which it is made. For example, metallic iron and gaseous oxygen are both elements, which cannot be reduced into simpler substances, but common iron rust, “ferrous oxide,” is a compound made up from iron and oxygen. Therefore, rust can be reduced to iron and oxygen, and rust can be created by combining iron and oxygen. But iron and oxygen are elements; they cannot be transformed into one another and are not composed of simpler or common materials.

Determining whether a pure substance is an element or a compound is a difficult and time-consuming process of experimentation. We will assume for our study that the elements have all been identified.

Since matter is anything that can have mass, we will spend much of our time in this study analyzing mass. Without proving it, we will assume the validity of the “Law of Conservation of Mass,” an experimental result that

simply says, “The total mass of all products of a chemical reaction is equal to the total mass of all reactants of the reaction.” In other words, matter cannot be created or destroyed by chemical or physical processes. This law makes it possible for us to measure masses of materials during reactions knowing that these masses aren’t variable or unpredictable.

With these assumptions in mind, we can proceed directly to experiments which led to the development of the Atomic Molecular Theory.

Observation 1: Mass Relationships during Chemical Reactions

Since matter is anything that has mass, then the Law of Conservation of Mass suggests that matter is also conserved during chemical reactions: whatever we start with, we wind up with, at least in total. However, this does not mean that matter must be made up of atoms. It simply says that matter is reorganized in some way to produce new substances with new properties when a reaction takes place.

Since we know that all substances are made of elements, then we can analyze the masses of the elements that participate in a chemical reaction. Most importantly, we can take a compound, break it into the elements that it is made of, and then find the masses of those elements. From the Law of Conservation of Mass, the total mass of the elements that make up the compound must equal the mass of the starting compound. For example, a particular compound called copper carbonate is composed of the elements copper, carbon, and oxygen. If we take a 100.0 g sample of copper carbonate, we find that it contains 51.5 g of copper, 38.8 g of oxygen, and 9.7 g of carbon. The total of these three masses is $51.5\text{ g} + 38.8\text{ g} + 9.7\text{ g} = 100.0\text{ g}$ and is the same as the mass of the copper carbonate.

This turns out to always be true. It does not matter what sample of copper carbonate we analyze, where it came from, who gave it to us, or how we made it. We always get these same masses of the element.

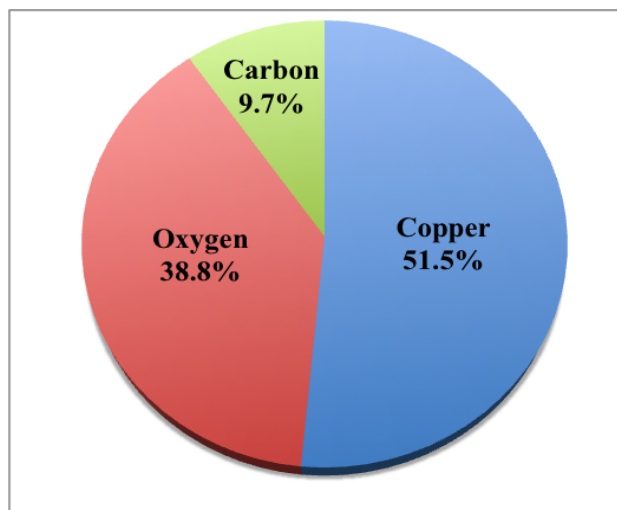
What if we take 200.0 g of copper carbonate instead? Experiments show us that we get 103.0 g of copper, 77.6 g of oxygen, and 19.4 g of carbon. The total of these three masses is $103.0\text{ g} + 77.6\text{ g} + 19.4\text{ g} = 200.0\text{ g}$, so again the

total mass is conserved. Even more importantly, there is something striking about these numbers when compared to the 100.0 g sample. When we double the mass of the copper carbonate, we also double the amount of copper it contains: 200.0 g of copper carbonate contains 103.0 g of copper, and 100.0 g of copper carbonate contains 51.5 g. The same is true for the amounts of oxygen and carbon.

One way to look at this is that the fraction of the copper carbonate which is copper is the same in both samples: 51.5 g/100.0 g is equal to 103.0 g/200.0 g, which is equal to 51.5%. This is a very important result. After looking at data from many experiments, we find that regardless of the specific sample of copper carbonate, regardless of the mass of that sample, and regardless of where that sample came from, the fraction of the mass of the sample which is copper is always the same, 51.5%. We get similar results for the oxygen and carbon. The fractions of the mass of every sample of copper carbonate are always 51.5% copper, 38.8% oxygen, and 9.7% carbon.



A sample of
copper carbonate
basic,
 $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$
illustrating the
blue-green color.



A graph showing ratios of components in copper carbonate
(photograph from
<http://woelen.homescience.net/science/chem/compounds/index.html>)

Other compounds show similar results. For example, every sample of the compound lead sulfide contains 86.7% lead and 13.3% sulfur by mass. This is true whether we take 1.00 g of lead sulfide or 1.00 kg of lead sulfide or any other total mass. We always get the same proportions of the masses of lead and sulfur in the sample.

This experimental observation is so consistent for the vast majority of all compounds that we regard it as a natural law, a summary of many, many observations that we therefore always expect to observe in future observations. In this case, the natural law we have observed is the Law of Definite Proportions:

Law of Definite Proportions: When two or more elements combine to form a compound, their masses in that compound are in a fixed and definite ratio.

This means that if we break a compound down into its elements and measure the masses of the elements that make it up, those masses are always in the same ratio.

We can illustrate this with a set of simple compounds each containing two of the elements of hydrogen, nitrogen, and oxygen. The definite ratios given by the Law of Definite Proportions are shown in [\[link\]](#) for 100.0 g of each compound:

Compound	Total Mass (g)	Mass of Hydrogen (g)	Mass of Nitrogen (g)	Mass of Oxygen (g)
Water	100.0	11.2	-	88.8
Ammonia	100.0	17.7	82.3	-
Nitric Oxide	100.0	-	46.7	53.3

Mass Relationships of Simple Compounds of Hydrogen, Nitrogen and Oxygen

Do these fixed masses mean that we are combining tiny particles of fixed mass together to form these compounds? To test this hypothesis, let's look at these numbers more closely to see if we can make any sense of them. One way to look at these data is to imagine taking a sample of water that contains exactly 1.00 g of hydrogen, and also a sample of ammonia that contains exactly 1.00 g of hydrogen. If we do this, the data now look as shown in the first two lines of [\[link\]](#).

Compound	Total Mass (g)	Mass of Hydrogen (g)	Mass of Nitrogen (g)	Mass of Oxygen (g)
Water	8.93	1.00	-	7.93
Ammonia	5.65	1.00	4.65	-
Nitric Oxide	2.14	-	1.00	1.14

Mass Relationships of Simple Compounds of Hydrogen, Nitrogen and Oxygen

Looking at the data this way allows us to compare how a fixed amount of hydrogen combines with either nitrogen or oxygen. From the Law of Definite Proportions, we know we will always get the fixed mass ratios shown in [\[link\]](#). We might imagine that this means that water is formed from 1 atom of hydrogen and 1 atom of oxygen, and that therefore the mass of 1 atom of oxygen is 7.93 times greater than the mass of 1 atom of hydrogen. If this is true, then ammonia might also be formed from 1 atom of hydrogen and 1 atom of nitrogen, in which case 1 atom of nitrogen has a mass 4.65 times greater than 1 atom of hydrogen.

This all seems consistent with the idea that these elements are made up of atoms combining in one-to-one ratios. But now we find a problem: if an atom of oxygen is 7.93 times as massive as an atom of hydrogen and if an atom of nitrogen is 4.65 times as massive as an atom of hydrogen, then it must be that an atom of oxygen is more massive than an atom of nitrogen by the ratio of $7.93/4.65 = 1.70$. When we now look at the third row of [\[link\]](#), the data tell us if nitric oxide is made up 1 atom of nitrogen and 1 atom of oxygen, an oxygen atom has a mass 1.14 times greater than the mass of a nitrogen. Our numbers and our conclusion aren't consistent with the experimental data, so we must have made an incorrect assumption.

One possibility is that we were wrong when we assumed that there are atoms of the three elements combining to form these three compounds. But

this does not seem likely, since it is hard to understand the fixed mass proportions without thinking that we are combining particles with fixed mass proportions.

Still, we must have made an incorrect assumption since our conclusions were contradictory. Recall that in doing our calculations of the masses of the atoms, we assumed that in each compound one atom of each element combined with one atom of the other element. Although this is a simple assumption, there is no reason why only one atom of each type might combine. Perhaps the ratios are different than this, and atoms combine in ratios of 1-to-2, 2-to-3, or any other simple combination. The problem that this poses is that we don't have a way to proceed from here. Even if we assume that the Law of Definite Proportions tells us that the elements are made up of atoms, we have no way to determine anything about these atoms. Without knowing the ratios of atoms in different compounds, we cannot determine the masses of the atoms of the elements. And without knowing the masses of the atoms of the elements, we cannot determine the ratios of the atoms in different compounds. Without knowing anything about the atoms of these elements, we do not have a basis for believing that these elements are made up of atoms. The Atomic Molecular Theory is still outside our reach. Without further observations, we cannot say for certain whether matter is composed of atoms or not.

Observation 2: Multiple Mass Ratios

We discovered above that we cannot conclude from the Law of Definite Proportions how many atoms of each element combine to form a particular compound, even if we assume that this is how a compound is formed. There is additional evidence that the Law of Definite Proportions is not final proof of the existence of atoms. It is easy to find different compounds with different chemical and physical properties, which are formed from the same two elements. This means that, if there are atoms, they can combine in many different ways.

For example, there are a huge number of simple “hydrocarbon” compounds formed just from hydrogen and carbon. [\[link\]](#) lists the mass percentages of just a few of these:

Compound	Total Mass(g)	Mass of Hydrogen(g)	Mass of Carbon(g)
Methane	100.0	25.1	74.9
Ethane	100.0	20.1	79.9
Benzene	100.0	7.7	92.3

Mass Relationships of Simple Compounds of Hydrogen and Carbon

The Law of Definite Proportions says that the ratio of the masses of two elements in a compound is fixed. In [\[link\]](#) we see several ratios of the masses of carbon and hydrogen. This is consistent with the Law of Definite Proportions, though, because each fixed ratio gives us a different compound with different chemical and physical properties. Therefore, different proportions of elements are possible, and depending on the elements, there may be one or many possible proportions and compounds. This is referred to as “multiple proportions.” Each compound gives us one definite proportion of the elements, but because there can be many compounds, there can be multiple different but definite proportions. [\[link\]](#) provides just three examples of compounds formed from carbon and hydrogen. The number of such compounds is huge, each with a different definite mass ratio and each with its own distinct physical and chemical properties. For example, methane gas is commonly burned in gas stoves and liquid octane is commonly used in cars; yet both are compounds of carbon and hydrogen only.

We will now look in great detail at a few compounds formed just from nitrogen and oxygen, simply called nitrogen oxides. Since we don’t know anything about these compounds, for now we’ll just call them Oxide A, Oxide B, and Oxide C. These three compounds are very different from one another. Two of these are quite toxic, but one is used as an anesthetic, particularly by dentists. Two of these are colorless, but one is a dark brown color. Let’s look at the mass ratios for these three compounds in [\[link\]](#).

Compound	Total Mass(g)	Mass of Nitrogen(g)	Mass of Oxygen(g)
Oxide A	100.0	30.5	69.5
Oxide B	100.0	46.7	53.3
Oxide C	100.0	63.7	36.3

Mass Relationships of Simple Compounds of Nitrogen and Oxygen

At first glance, there is nothing special about these numbers. There are no obvious patterns or relationships amongst the masses or mass ratios. But let's look at this data in the same way as we did in [\[link\]](#) by finding the mass of oxygen that combines with 1.00 g of nitrogen. This is in [\[link\]](#).

Compound	Total Mass(g)	Mass of Nitrogen(g)	Mass of Oxygen(g)
Oxide A	3.28	1.00	2.28
Oxide B	2.14	1.00	1.14
Oxide C	1.57	1.00	0.57

Mass Relationships of Simple Compounds of Nitrogen and Oxygen

You might have to look at these data very hard to see it, but there is a pattern that is obvious once you see it. In the column for the Mass of Oxygen, the three values listed have a simple relationship: each one is a multiple of 0.57. We can see this most clearly if we divide each of the

masses for the three oxides by 0.57. This shows us that the ratio 2.28 : 1.14 : 0.57 is equal to the ratio 4 : 2 : 1.

What does this tell us? It means that if we have a fixed mass of nitrogen, the mass of oxygen which will combine with it cannot be simply any amount. In fact, the opposite is true. There are a few specific masses of oxygen which will combine with the fixed nitrogen, and those specific masses are integer multiples of a fixed unit of mass. It is particularly interesting that the masses of oxygen are in integer ratios. Integers are a special set of numbers used for one primary purpose, which is to count objects. In this case, the “object” must be a fixed unit of mass of oxygen.

The data in [\[link\]](#) tell us that when we have a fixed amount of nitrogen, it can be combined only with some integer number of a fixed unit of mass of oxygen. Why would there be a fixed unit of mass of oxygen? The simplest and best explanation is that oxygen exists as fixed units of mass, or particles, and we call these particles “atoms” of oxygen. Thus, the data in [\[link\]](#) lead us to a conclusion that the element oxygen is composed of individual atoms with identical mass. We have shown that matter is made up of particles and that elements consist of identical particles or atoms.

We can see these simple integer ratios in other compounds, as well. Let’s look back at [\[link\]](#), which shows compounds of carbon and hydrogen. The ratios of the masses don’t appear to be interesting until we do the same type of analysis that we did on the nitrogen oxides. Let’s fix the mass of hydrogen in each of these compounds and find out the masses of carbon. The results are in [\[link\]](#).

Compound	Total Mass(g)	Mass of Hydrogen(g)	Mass of Carbon(g)
Methane	3.98	1.00	2.98

Ethane	4.97	1.00	3.97
Benzene	12.99	1.00	11.99

Mass Relationships of Simple Compounds of Hydrogen and Carbon

The ratio 2.98 : 3.97 : 11.99 is the same as the ratio 3 : 4 : 12. Once again for a fixed amount of hydrogen, the mass of carbon that can combine is a multiple of a fixed mass unit. Therefore, carbon can only react in small fixed units of mass, so carbon is made up of atoms. These data also show the same conclusion for hydrogen. All we have to do is fix the carbon mass and compare the masses of hydrogen that will combine with that amount of carbon.

The observations we have made for carbon and hydrogen compounds and nitrogen and oxygen compounds are general. They apply to all simple compounds. Thus, we state a new natural law which summarizes these observations, the Law of Multiple Proportions:

Law of Multiple Proportions: When two elements combine to form more than one compound, the masses of one element that combine with a fixed mass of the other element are in simple integer ratio.

The Law of Multiple Proportions is rather wordy and difficult to state, but the data in [\[link\]](#) and [\[link\]](#) illustrate it clearly. If we fix the mass of one element, the masses of the other element in the three compounds are always in a simple integer ratio. Since these observations are general, then the conclusions that follow are also general: all elements are made up of fixed units of mass, and we call these particles “atoms.”

These conclusions point to other very important conclusions, as well. Since compounds are formed from the elements, then compounds consist of atoms of the elements in various combinations. Very importantly, the integer ratios of the masses of the atoms are always simple, that is, small integers. Therefore, the atoms of the different elements combine in simple ratios, too. This means that the small particles called atoms are combining in simple ways to form small particles of the compound. We call these particles

“molecules,” and compounds consist of identical molecules made up of atoms in simple integer ratios.

The Atomic Molecular Theory: We have now observed experimental data which reveal to us several important conclusions. We call these conclusions “postulates,” and taken together these postulates form the Atomic Molecular Theory:

1. Each element is composed of very small, identical particles called atoms.
2. All atoms of a single element have the same characteristic mass.
3. The number and masses of these atoms do not change during a chemical transformation.
4. Each compound consists of identical molecules, which are small, identical particles formed of atoms combined in simple whole number ratios.

At this point, we know very little about these atoms, other than that they exist, have fixed mass for each element, and combine to form molecules. We don't know what the atomic masses are, even in comparison to each other, and we don't know the simple integer ratios by which they combine to form molecules and compounds. We have made a major step forward in proving that matter is made up of atoms and molecules, but we have a long way to go to make this theory useful.

Review and Discussion Questions

1. Assume that matter does not consist of atoms. Show by example how this assumption leads to hypothetical predictions which contradict the Law of Multiple Proportions. Do these hypothetical examples contradict the Law of Definite Proportions? Are both observations required for confirmation of the atomic theory?
2. Two compounds, A and B, are formed entirely from hydrogen and carbon. Compound A is 80.0% carbon by mass, and 20.0% hydrogen, whereas Compound B is 83.3% carbon by mass and 16.7% hydrogen. Demonstrate that these two compounds obey the Law of Multiple

- Proportions. Explain why these results strongly indicate that the elements carbon and hydrogen are composed of atoms.
3. In many chemical reactions, mass does not appear to be a conserved quantity. For example, when a tin can rusts, the resultant rusty tin can has a greater mass than before rusting. When a candle burns, the remaining candle has invariably less mass than before it was burned. Provide an explanation of these observations, and describe an experiment which would demonstrate that mass is actually conserved in these chemical reactions.
 4. The following question was posed on an exam:

An unknown non-metal element (Q) forms two gaseous fluorides of unknown molecular formula. A 3.2 g sample of Q reacts with fluorine to form 10.8 g of the unknown fluoride A. A 6.4 g sample of Q reacts with fluorine to form 29.2 g of unknown fluoride B. Using these data only, demonstrate by calculation and explanation that these unknown compounds obey the Law of Multiple Proportions.

A student responded with the following answer:

The Law of Multiple Proportions states that when two elements form two or more compounds, the ratios of the masses of the elements between the two compounds are in a simple whole number ratio. So, looking at the data above, we see that the ratio of the mass of element Q in compound A to the mass of element Q in compound B is $3.2:6.4 = 1:2$, which is a simple whole number ratio. This demonstrates that these compounds obey the Law of Multiple Proportions.

Assess the accuracy of the students answer. In your assessment, you must determine what information is correct or incorrect, provide the correct information where needed, explain whether the reasoning is logical or not, and provide logical reasoning where needed.

By John S. Hutchinson, Rice University, 2011

Atomic Masses and Molecular Formulas

Introduction

In this study, our goals are to determine the masses of the atoms of each element and to find the ratios of the atoms that combine to form the molecules of different compounds. We will find that we determine the atomic masses relative to one another. In other words, we will find that the atoms of one element may be 1.2 times as massive as the atoms of another element. We will not actually determine the mass of an atom relative to, say, a large sample of matter like a bar of metal or a glass of water. For almost all purposes in Chemistry, it turns out that we only need these relative masses. We will also find the formulas of individual molecules for different compounds. The “molecular formula” tells us how many atoms of each type there are in a molecule of a compound. For example, many people know that water is H_2O , meaning that a molecule of water contains two hydrogen atoms and one oxygen atom. Although we haven’t shown it yet, the molecular formula of water is H_2O .

The postulates of the Atomic Molecular Theory provide us a great deal of understanding of pure substances and chemical reactions. For example, the theory reveals the distinction between an element and a compound. In an element, all atoms are identical. In a compound, there are atoms of two or more elements combined into small identical molecules in small integer ratios. The theory also reveals to us what happens during a chemical reaction. When two elements react, their atoms combine to form molecules in fixed ratios, making a new compound. When two compounds react, the atoms in the molecules of these reactant compounds recombine into new molecules of new product compounds.

As good as this is, it is about as far as we can go without further observations and analysis. We don’t know the relative masses of the atoms, and we don’t know the molecular formula for any compound. It turns out that to know one of these things we need to know the other one.

To see this, let’s take another look at the data in the [Concept Development Study on Atomic Molecular Theory](#). Here it is again as [\[link\]](#):

Compound	Total Mass (g)	Mass of Nitrogen (g)	Mass of Oxygen (g)
Oxide A	3.28	1.00	2.28
Oxide B	2.14	1.00	1.14
Oxide C	1.57	1.00	0.57

Mass Relationships of Simple Compounds of Nitrogen and Oxygen

We now know that a fixed mass of nitrogen means a fixed number of nitrogen atoms, since each atom has the same mass. And if we double the mass of oxygen, we have doubled the number of oxygen atoms. So, comparing Oxide A to Oxide B, for the same number of nitrogen atoms, Oxide A has twice as many oxygen atoms as Oxide B, which has twice as many oxygen atoms as Oxide C.

There are many possible molecular formulas which are consistent with these ratios. To see this, we can show that any one of the oxides A, B, or C could have the molecular formula NO. If Oxide C has the molecular formula NO, then Oxide B has the formula NO₂, and Oxide A has the formula NO₄. If Oxide B has molecular formula NO, then Oxide A has formula NO₂, and Oxide C has formula N₂O. It might not be clear that Oxide C would be N₂O. The mass data tell us that Oxide B has twice as many oxygen atoms *per nitrogen atom* as Oxide C. So if Oxide B and Oxide C have the same number of oxygen atoms, then Oxide C has twice as many nitrogen atoms as Oxide B. As a similar example, if Oxide A has formula NO, then Oxide B has formula N₂O and Oxide C has formula N₄O. These three possibilities are listed in [\[link\]](#).

Assuming	Oxide C is	Oxide B is	Oxide A is
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that:	NO	NO	NO
Oxide A is	NO ₄	NO ₂	NO
Oxide B is	NO ₂	NO	N ₂ O
Oxide C is	NO	N ₂ O	N ₄ O

Possible Molecular Formulae for Nitrogen Oxides

We don't have a way to know which of these sets of molecular formulas are right, since all three sets are consistent with the data we have. How can we pick the right one? If we had some way to "count" the numbers of atoms in a sample of each compounds, then we would know. This sounds quite difficult, though. On the other hand, if we knew that the ratio of the mass of an nitrogen atom to an oxygen atom is 2.28:1.00, which is the mass ratio in Oxide A, then we could know that Oxide A is NO. But we don't have a way to take the mass of an individual atom, even on a relative basis.

What we have learned is that, if we know the relative masses of the atoms, we can determine molecular formulas. And if we know the molecular formulas, we can determine relative atomic masses. We need one or the other to move forward.

Foundation

We are assuming that we know the postulates of the Atomic Molecular Theory, as developed in the first Concept Development Study. These are: (1) the elements are comprised of identical atoms; (2) all atoms of a single element have the same characteristic mass; (3) the number and masses of these atoms do not change during a chemical transformation; and (4) compounds consist of identical molecules formed of atoms combined in simple whole number ratios. We will base much of our work on the observed natural laws on which our theory is based: the Law of Conservation of Mass, the Law of Definite Proportions, and the Law of Multiple Proportions.

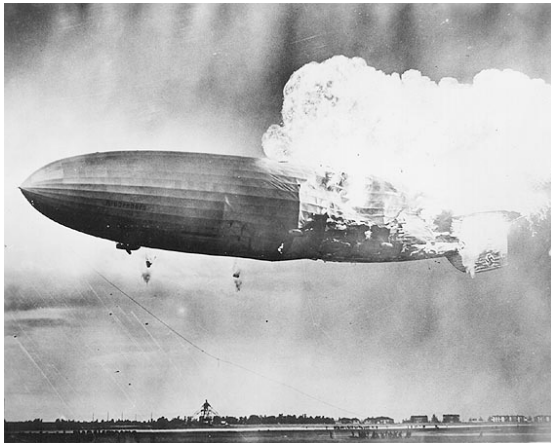
We will be making observations about the physical properties of gas samples, particularly the volumes of gases measured under conditions with a fixed temperature and a fixed pressure. We will not need much technical information about temperature and pressure. For now, we will simply stick with the common understanding that temperature is a measure of how hot or cold a sample of a substance is. Temperature can be measured by a thermometer, which is any kind of gadget which gives us the same value for two objects that are in contact with each other so that they have the same temperature. Pressure is a measure of what is sometimes called the “spring of air,” which is the force with which a gas resists compression. There are a number of ways to measure pressure, but we will only need to know that we have a way to take measurements on gas samples such that they have the same pressure.

Observation 1: Volumes of Gases during Chemical Reactions

During chemical reactions, some chemical and physical properties such as the total mass of the materials remain unchanged, but most properties do change. We commonly observe changes in properties when new materials are made. For example, products of reactions in comparison to the reactants may appear harder or softer, more or less colorful, more or less brittle, and more or less dense. For gases that react, volume is one of those properties that is not always conserved. A famous explosive reaction of gases involves the burning of hydrogen gas in oxygen gas to form water vapor, as shown in Figures 1 and 2. If 1 liter of oxygen gas reacts with 2 liters of hydrogen gas, the product water vapor will occupy 2 liters with no hydrogen or oxygen gas left over. (This is true if the volumes are measured with all gases at the same temperature and pressure.) Notice that the total volume of gases is not conserved: the combined volume of the reactants is 3 liters, but the volume of the product is 2 liters.



Demonstration of an
exploding balloon containing
hydrogen and oxygen done at
Rice University by Dr. Mary
McHale
(<http://chemistry.rice.edu/>).



The Hindenburg, a German
passenger airship, bursting into
flames in 1937
(<http://www.nlhs.com/tragedy.htm>)

There is, however, something striking about the data just given for reaction of hydrogen and oxygen that should cause us to take a closer look the property of volume: the volumes of the gases are in simple integer ratios. This might look like a simple consequence of our choosing to react 1 liter of oxygen with 2 liters of hydrogen. But we can take any volumes we want, not just integer number of liters. We can react 1.42 liters of oxygen with 2.84 liters of hydrogen, and all of the hydrogen and oxygen will be consumed to form 2.84 liters of water vapor. Notice that the ratio of volumes is oxygen:hydrogen:water vapor = 1:2:2, a simple integer ratio. If we try to react a different ratio, like 1.42 liters of oxygen with 3.00 liters of hydrogen, there will be leftover hydrogen when the reaction is complete. This is one way of observing the Law of Definite Proportions. We cannot choose to react arbitrary amounts of hydrogen and oxygen, since they combine in a fixed ratio by mass.

We thus observe that the volumes of hydrogen and oxygen that react, as well as the volume of water vapor product, are in a simple integer ratio. The only requirement for this to be true is that all of the gas volumes are measured with the same temperature and pressure. This result is quite general when we observe chemical reactions involving gases. The volume of hydrogen that will react with 1.0 L (liters) of nitrogen is 3.0 L, and the product of the reaction ammonia gas has volume 2.0 L. The ratio of volumes is a simple set of integers. Hydrogen chloride gas is formed from reacting hydrogen gas with chlorine gas, and again, 1.0 L of chlorine will only react with 1.0 L of hydrogen gas, with no hydrogen or chlorine left over and with 2.0 L of hydrogen chloride gas produced.

Many, many such observations can be made leading us to a general law of nature called the Law of Combining Volumes:

Law of Combining Volumes: When gases combine during a chemical reaction at fixed temperature and pressure, the volumes of the reacting gases and products are in simple integer ratios.

Avogadro's Law – Counting Particles

The integer ratios in the Law of Combining Volumes are very striking. There are few quantities in nature which are measured in integers, so it is always surprising and revealing to discover integers in measurements. Integers are generally measured only when we are counting particles or taking ratios of particles. Observing volumes in simple integer ratios should be very revealing.

Looking back at the data for hydrogen and oxygen, we see that the volumes are in a simple 2:1 ratio. One of our major conclusions expressed in the Atomic Molecular Theory is that atoms and molecules react in simple integer ratios. A possible explanation of the integer volume ratios is that these are the same integer ratios as the particles react in. In the hydrogen-oxygen case, this means that the ratio of hydrogen atoms to oxygen atoms reacting is 2:1, since the volume ratio is 2:1.

If the volumes are in a 2:1 ratio and the particles are in a 2:1 ratio, then a powerful conclusion emerges: equal volumes of the two gases must contain equal numbers of particles, regardless of whether they are hydrogen or oxygen. This seems like quite a leap to make, since we are concluding something about the numbers of particles without ever having counted them. What is the basis for this leap of logic? The most important part of the reasoning is the uniqueness of the integers. It is hard to come up with a simple explanation for why gas volumes should only react in integer ratios. The only simple conclusion is the one we have come to and that was first stated by Avogadro:

Avogadro's Law: Equal volumes of gas contain equal numbers of particles, if the volumes are measured at the same temperature and pressure.

One way to come to this conclusion is to imagine that it is not true. Assume that equal volumes of gases do not contain equal numbers of particles and instead contain unrelated numbers of particles. Let's assume for example that 1 L of gas A contains 3.14 times as many particles as 1 L of gas B. Then to take equal numbers of A and B particles, we would need 3.14 L of gas B for every 1 L of gas A. For the gas particles of A and B to react in a simple integer ratio of particles, we would then need a non-integer ratio of volumes. But this is not what is observed in the Law of Combining Volumes: the volume of A and B that react are always observed to be a

simple integer ratio. Our assumption that equal volumes contain unrelated numbers of particles leads us to a conclusion that is contradicted by experiments, so our assumption must be wrong. Therefore, equal volumes of gases contain equal numbers of particles. We can conclude that Avogadro's Law follows logically from the Law of Combining Volumes.

There is a problem that we have to work out. Looking back at one piece of evidence that led us to the Law of Combining Volumes, we found that 1 L of hydrogen plus 1 L of chlorine yields 2 L of hydrogen chloride. Using the conclusion of Avogadro's Law, the volume ratio and the particle ratio must be the same. This seems to say that 1 hydrogen atom plus 1 chlorine atom makes 2 hydrogen chloride molecules. But this can't be! How could we make 2 identical molecules of hydrogen chloride from a single chlorine atom and a single hydrogen atom? This would require us to divide each hydrogen and chlorine atom, violating the postulates of the Atomic Molecular Theory.

There is one solution to this problem, as was recognized by Avogadro. We have to be able to divide a hydrogen gas particle into two identical pieces. This means that a hydrogen gas particle must contain an even number of hydrogen atoms, most simply, two. This says that hydrogen gas exists as hydrogen molecules, and each hydrogen molecule contains two hydrogen atoms. The same conclusions apply to chlorine: a chlorine gas molecule must contain two chlorine atoms. If these conclusions are correct, then one hydrogen molecule, H_2 , can react with one chlorine molecule, Cl_2 , to form two hydrogen chloride molecules, HCl . The ratio of the reactant particles and the product particles is then the same as the ratio of the reactant gas volumes and the product gas volumes.

This is a wonderful result because we have now determined the molecular formula of hydrogen chloride, HCl . We have found a way to "count" the numbers of atoms in the reaction, at least in ratio, by measuring the volumes of the gases that react and that are produced. This gives us a chemical reaction showing the atoms and molecules that participate in the reaction in the correct ratio:

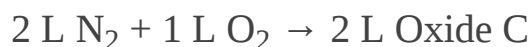
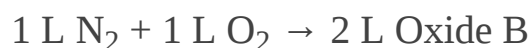
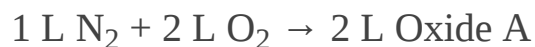


This chemical equation is consistent with all of our known observations and the postulates of the Atomic Molecular Theory.

Since the Law of Combining Volumes is a general result, we can look at many chemical reactions with the same analysis. Let's apply this to the hydrogen and oxygen reaction discussed earlier. Remember that 2 L of hydrogen react with 1 L of oxygen to form 2 L of water vapor. This means that two particles of hydrogen (which we know to be H_2) react with one particle of oxygen to form two particles of water. Once again, we have the problem that one atom of oxygen cannot make two molecules of water. Therefore, an oxygen gas particle cannot be an oxygen atom, so oxygen gas exists as oxygen molecules, O_2 . Since two H_2 molecules react with one O_2 molecule to form two water molecules, each water molecule must be H_2O . We can write the chemical equation:



We can use these observations to finally solve the riddle which is posed in [\[link\]](#). We need to observe the volumes of oxygen and nitrogen which react to form Oxides A, B, and C. In separate experiments, we find:



(At this point, it is pretty clear from the data and using our previous reasoning that nitrogen gas must consist of nitrogen molecules, N_2 , since 1 L of nitrogen gas can make 2 L of Oxide B.) From these data, we can conclude that Oxide B has molecular formula NO , since 1 L of oxygen plus 1 L of nitrogen produces 2 L of Oxide B with nothing left over. Similarly and with the use of [\[link\]](#), we can say that Oxide A is NO_2 and Oxide C is N_2O .

Observation 2: Relative Atomic Masses

In the Introduction, we presented a dilemma in developing the Atomic Molecular Theory. To find the molecular formula of a compound, we needed to find the relative atomic masses. And to find the relative atomic masses, we needed to find the molecular formula of a compound. Using Avogadro's Law, we have found a way to break out of this dilemma. By measuring gas volumes during reactions, we can essentially count the numbers of atoms in a molecule, giving us the molecular formula. Our task now is to use this information to find atomic masses.

We can begin by looking at the data in [\[link\]](#) and focusing on Oxide B at first. We know now that Oxide B has molecular formula NO. As such, it is given the name Nitric Monoxide, or more commonly Nitric Oxide. We also know from [\[link\]](#) that the mass ratio of oxygen to nitrogen in NO is 1.14 to 1.00. Since there are equal numbers of nitrogen atoms and oxygen atoms in any sample of NO, then the mass ratio of an oxygen atom to a nitrogen atom is also 1.14 to 1.00. Stated differently, an oxygen atom has mass 1.14 times greater than a nitrogen atom.

This is a good start, but now we need more elements. To bring in hydrogen, we can analyze the data from [\[link\]](#) in the first Concept Development Study which gives the mass ratio of oxygen and hydrogen in water. That data shows that the mass ratio of oxygen to hydrogen is 7.93 to 1.00. But we found in the previous section that the molecular formula of water is H₂O. This means that in a sample of water there are twice as many hydrogen atoms as there are oxygen atoms. Therefore, the ratio of the mass of one oxygen atom to one hydrogen atom must be 7.93 to 0.50, or 15.86 to 1.00.

These atomic mass ratios need to be consistent with each other, since the masses of the atoms of an element are always the same. So if the ratio of one hydrogen to one oxygen is 1.00 to 15.86, and the ratio of one nitrogen to one oxygen is 1.00 to 1.14, then the ratio of one hydrogen to one nitrogen must be 1.00 to 13.91. We should be able to check this by looking at the hydrogen-nitrogen compound ammonia, also listed in [\[link\]](#) of the previous Concept Development Study. There we find that the mass ratio of nitrogen to hydrogen is 4.65 to 1.00. Clearly, ammonia is not NH. To find the molecular formula of ammonia, we need data from the Law of Combining Volumes. Experimental data reveal that 1 L of N₂ reacts with 3 L of H₂ to

produce 2 L of ammonia. From this, we should be able to conclude that an ammonia molecule has the molecular formula NH_3 . Therefore, in a sample of ammonia, there are three times as many hydrogen atoms as there are nitrogen atoms. This means that the ratio of the mass of a nitrogen atom to a hydrogen atom is 3×4.65 to 1.00, or 13.95 to 1.00. We now have enough data to say that hydrogen, nitrogen, and oxygen atoms have mass ratio of 1.00:13.95:15.86.

Observation 3: Atomic Masses for Non-Gaseous Elements

The next element we would certainly like to have an atomic mass for would be carbon, and we would certainly like to be able to determine molecular formulas for carbon containing compounds. We have data from [\[link\]](#) in the previous CDS on compounds of hydrogen and carbon. But our analysis is not going to work this time. The Law of Combining Volumes and Avogadro's Law in combination allow us to count atoms and find molecular formulas, but only for elements and compounds which are gases. Carbon is not a gas. It exists in several different elemental forms, but all are solid at normal temperatures and even at very high temperatures.

This means that we need to work harder and add some additional observations to our work. Let's start with the two most common oxides of carbon, which for now we will give the names Oxide A and Oxide B. (Their real names, carbon monoxide and carbon dioxide, are based on assuming that we already know their molecular formulas. But we don't know these, so we'll stick with these code names for now.) Here are the data for the mass relationships from the Law of Multiple Proportions:

Compound	Total Mass (g)	Mass of Carbon (g)	Mass of Oxygen (g)
Oxide A	2.33	1.00	1.33

Oxide B	3.66	1.00	2.66
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Mass Relationships of Simple Compounds of Carbon and Oxygen

It is clear to see the Law of Multiple Proportions here since Oxide B has exactly twice the mass of Oxide A for the same mass of carbon. Now we would like to observe the Law of Combining Volumes and apply Avogadro's Law, but carbon is not a gas. But we can at least look at the ratios of the volume of oxygen and the volume of the oxides produced. For Oxide A, 1 L of oxygen will produce 2 L of Oxide A. For Oxide B, 1 L of oxygen will produce 1 L of Oxide B. From these data, we can see that an Oxide A molecule contains one oxygen atom, since a single O_2 molecule makes two Oxide A molecules. We can also see that an Oxide B molecule contains two oxygen atoms, since a single O_2 molecule produces a single Oxide B molecule.

Now we know part of the molecular formulas each of the oxides, but we don't know the number of carbon atoms in each. Oxide A could be CO , C_2O , C_3O , etc., and Oxide B could be CO_2 , C_2O_2 , etc. Our only way to proceed is with Avogadro's Law. We can use this to determine the relative mass of each oxide molecule, even if we can't determine the relative mass of the carbon atoms. The mass of 1 L of Oxide A is less than the mass of 1 L of oxygen. This is because, even though equal volumes contain the same number of particles, the particles themselves have different masses. In fact, since 1 L of each gas contains the same number of particles, then the mass ratio of 1 L of Oxide A to oxygen is exactly the same as the mass ratio of one Oxide A molecule to one oxygen molecule. An experimental measurement shows that the mass of 1 L of Oxide A is 87.5% of the mass of 1 L of oxygen. So the mass of one particle of Oxide A must be 87.5% of the mass of an O_2 molecule. On the relative scale found in the previous section, the mass of one oxygen molecule is $15.86 \times 2 = 31.72$. So a particle of Oxide A must have relative mass $0.875 \times 31.72 = 27.76$. Remember though that an Oxide A contains just one oxygen atom. So, of this relative mass, 15.86 belongs to the oxygen atom, leaving 11.90 for the carbon.

Is this the relative mass of a carbon atom? We don't know because we don't know whether a molecule of Oxide A contains 1, 2, or 3 atoms of carbon

(or for that matter, any number). What we can say is that the mass of a carbon atom is either 11.9, one-half of that, one-third of that, or some integer fraction of that depending on how many carbon atoms are in Oxide A.

How can we determine the right number? The answer is found from persistence. We can repeat this same measurement and calculation for Oxide B. The mass of 1 L of Oxide B is 1.375 times greater than the mass of 1 L of oxygen. Therefore, one particle of Oxide B has relative mass 43.59. But Oxide B molecules contain two oxygen atoms, so the part of this mass which is carbon is 43.59 minus the relative mass of the two oxygen atoms. This gives the mass of carbon in Oxide B as 11.9. This is the same mass of carbon that we found in Oxide A. Therefore, Oxide A and Oxide B have exactly the same number of carbon atoms. Perhaps, the number of carbon atoms in each is just one, but we can't be sure from this data.

To convince ourselves, we should repeat this process for many gaseous compounds of carbon, including ones that contain hydrogen and oxygen both. In every experiment, we find that the relative mass of carbon in each molecule is either 11.9 or a simple multiple of 11.9. It is never less than 11.9. We can conclude that the relative mass of a carbon atom on the same scale we have been using is 11.9. We can also conclude that Oxide A and Oxide B each contain one carbon atom, so the molecular formulas of Oxide A and Oxide B are CO and CO₂.

This procedure can be used to find molecular formulas of compounds containing other non-gaseous elements. This is the actual procedure that was used around 1850 to provide the first set of relative atomic masses and the first definite molecular formulas for common compounds. This is a major stride forward from the postulates of the Atomic Molecular Theory.

As one last step, we note that the standard agreed on by chemists for the relative atomic masses does not take hydrogen to have mass 1.00. Rather, on the agreed upon scale, the relative atomic mass of hydrogen is 1.008, that of carbon is 12.01, that of nitrogen is 14.01, and that of oxygen is 15.999. These ratios are the same as the ones we observed in our calculations.

Chemical Algebra: Stoichiometry

In the [Introduction](#), we decided that we could determine molecular formulas if we knew the relative atomic masses. At that point, we didn't have the relative atomic masses, but now we do. Once we know all the relative atomic masses, we no longer need the Law of Combining Volumes and Avogadro's Law to determine molecular formulas.

Let's show this by an example, with a compound which contains only carbon, oxygen, and hydrogen. An analysis from the Law of Definite Proportions gives us that the compound is 40.0% carbon, 53.3% oxygen, and 6.7% hydrogen by mass. In other words, if we have a 100.0 g sample of the compound, it consists of 40.0 g of carbon, 53.3 g of oxygen and 6.7 g of hydrogen. But we also know that the relative masses of carbon, oxygen, and hydrogen are 12.01:15.99:1.008. This will allow us to determine the relative numbers of atoms of each type in the compound.

To do this, we create a method of chemical algebra. Let's start by assuming that we have exactly N atoms of carbon, N atoms of hydrogen, and N atoms of oxygen. N is some very large number, and it doesn't matter what it is, as long as we have taken the same N for all three elements. The relative mass of 1 carbon atom to 1 hydrogen atom is 12.01 to 1.008. Therefore the relative mass of N carbon atoms to N hydrogen atoms is also 12.01 to 1.008. Let's pick a very specific N : let's make N be whatever number it is such that that a sample of N carbon atoms has mass 12.01g. Interestingly, we don't need to know what N is – we just need to find a sample of carbon which has a mass of 12.01 g.

What is the mass of N hydrogen atoms (for the exact same N)? It must be 1.008 g, since each hydrogen atom has mass ratio to each carbon atom 1.008 to 12.01. Therefore, if we weigh out a sample of carbon with mass 12.01 g and a sample of hydrogen with mass 1.008 g, we know that we have exactly the same number of atoms of each type.

Since this seems like a useful number of atoms, we will give it a name. N is called a mole of atoms. We don't need to know what N is to know that we can find a mole of atoms simply by finding the mass of a sample: 12.01 g of carbon, 1.008 g of hydrogen, 15.99 g of oxygen, and so on. (For historical

reasons, the value of N which is a mole of atoms is called “Avogadro’s number,” in his honor but not because he discovered the number.

Avogadro’s number is given the symbol N_A . The number of particles in a mole is approximately 6.022×10^{23} , although we will almost never need this number when doing chemical calculations.)

Since we know the mass of one mole of a substance, we can find the number of moles in a sample of that substance just by finding the mass. Consider a sample of carbon with mass 24.02 g. This is twice the mass of one mole, so it must contain twice the number of particles as one mole. This must be two moles of particles. That example was easy, but what if we have 30.02 g of carbon? Since one mole has mass 12.01 g, then 30.02 g must contain $30.02/12.01$ moles = 2.5 moles. Even more generally, then, if we have a sample of an element has mass m and the atomic mass of the element is M , the number of moles of atoms, n , is

$$n = \frac{m}{M}$$

Since one mole contains a fixed number of particles, regardless of the type of particle, calculating the number of moles n is a way of counting the number of particles in a sample with mass m . For example, in the 100.0 g sample of the compound above, we have 40.0 g of carbon, 53.3 g of oxygen, and 6.7 g of hydrogen. We can calculate the number of moles of atoms of each element using the equation above:

$$n_C = \frac{40.0\text{g}}{12.0\text{g/mol}} = 3.33\text{moles}$$

$$n_O = \frac{53.3\text{g}}{16.0\text{g/mol}} = 3.33\text{moles}$$

$$n_H = \frac{6.7\text{g}}{1.0\text{g/mol}} = 6.67\text{moles}$$

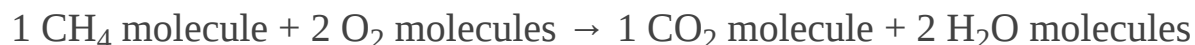
A mole is a fixed number of particles. Therefore, the ratio of the numbers of moles is also the same as the ratio of the numbers of atoms. In the data above, this means that the ratio of the number of moles of carbon, oxygen, and hydrogen is 1:1:2, and therefore the ratio of the three types of atoms in

the compound is also 1:1:2. This suggests that the compound has molecular formula COH_2 .

However, this is just the ratio of the atoms of each type, and does not give the number of atoms of each type. Thus the molecular formula could just as easily be $\text{C}_2\text{O}_2\text{H}_4$ or $\text{C}_3\text{O}_3\text{H}_6$. Since the formula COH_2 is based on empirical mass ratio data, we refer to this as the empirical formula of the compound. To determine the molecular formula, we need to determine the relative mass of a molecule of the compound, i.e. the molecular mass. One way to do so is based on the Law of Combining Volumes, Avogadro's Hypothesis, and the Ideal Gas Law. To illustrate, however, if we were to find that the relative mass of one molecule of the compound is 60.0, we could conclude that the molecular formula is $\text{C}_2\text{O}_2\text{H}_4$.

Counting the relative number of particles in a sample of a substance by measuring the mass and calculating the number of moles allows us to do "chemical algebra," calculations of the masses of materials that react and are produced during chemical reactions.

This is easiest to see with an example. Some of the most common chemical reactions are those in which compounds of hydrogen and carbon, called hydrocarbons, are burned in oxygen gas to form carbon dioxide and water. The simplest hydrocarbon is methane, and using the methods of this study, we can find that methane has the molecular formula, CH_4 . The chemical equation which represents the burning of methane is:



It is important to note that the number of atoms of each type is conserved during the chemical reaction. The reactants and products both contain 1 carbon atom, 4 hydrogen atoms, and 2 oxygen atoms. This is called a "balanced" chemical equation, and it expresses the postulate of the Atomic Molecular Theory that the numbers of atoms of each element does not change during a chemical reaction.

In chemical algebra, we can ask and answer questions such as, "If we burn 1.0 kg of methane, what is the mass of carbon dioxide which is produced?" Such a question would clearly be of importance in understanding the

production of greenhouse gases like CO₂. The chemical equation above expresses a relationship between the number of molecules of methane which are burned and the number of molecules of CO₂ produced. From the equation, each molecule of CH₄ produces one molecule of CO₂. Therefore, if we knew how many molecules of CH₄ we have in a sample, we know how many molecules of CO₂ we will produce.

The chemical equation works for any number of molecules. If we burn N molecules of CH₄, we produce N molecules of CO₂. This will work no matter what N is. Therefore, we can say that 1 mole of CH₄ molecules will produce 1 mole of CO₂ molecules. The chemical equation works just as well for moles as it does for molecules, since 1 mole is just a fixed number of molecules. And we know how to calculate the number of moles from a measurement of the mass of the sample.

Recall that we are interested in what happens when we burn 1.00 kg = 1000 g of methane. We just need to know the mass of a mole of methane. Since one molecule of methane has relative mass 16.0, then one mole of methane has mass 16.0 g/mol. Then the number of moles in 1000 g of methane can be calculated by dividing by the mass of 1.0 mole of methane:

$$n_{CH_4} = \frac{1000g}{16.0g/mol} = 62.5moles$$

This means we have counted the number of particles of CH₄ in our sample. And we know that the number of particles of CO₂ produced must be the same as this, because the chemical equation shows us the 1:1 ratio of CH₄ to CO₂. So, 62.5 moles of CO₂ are produced by this reaction and this 1.0 kg sample.

We are usually more interested in the mass of the product, and we can calculate this, too. The mass of one mole of CO₂ is found from the mass of one mole of C and two moles of O, and is therefore 44.0 g. This is the mass for one mole. The mass for 62.5 moles will be

$$m_{CO_2} = n_{CO_2} M_{CO_2} (62.5moles)(44.0g/mol) = 2750g = 2.75kg$$

Therefore, for every 1 kg of methane burned, we produce 2.75 kg of CO₂.

The important conclusion from this example of chemical algebra is that it is possible to calculate masses of products from masses of reactants. We do so by using a balanced chemical equation and by understanding that the equation gives us the ratio of moles of reacting materials just as it gives us the ratio of molecules of reacting materials. This is because numbers of moles and numbers of molecules are simply different ways of counting the number of particles.

Chemical algebra is usually referred to as “stoichiometry,” a somewhat intimidating term that makes the calculations seem harder and more abstract than they are. We really only need to remember two things. First, from the Atomic Molecular Theory, a chemical reaction can be represented by a balanced chemical equation which conserves the numbers of atoms of each element. Second, the balanced equation provides the ratio of the number of product molecules to the number of reactant molecules, either in numbers of molecules or numbers of moles. Thus, we can solve problems efficiently by calculating the number of moles.

A final interesting note about Avogadro’s number is helpful in understanding what 1 mole is. A question often asked is, where did the number 6.022×10^{23} come from? If we wanted to pick a very large number for the number of particles in a mole, why didn’t we pick something easier to remember, like 6×10^{23} , or even 1×10^{23} ? The value of Avogadro’s number comes from the fact that we chose 1 mole to be the number of carbon atoms in 12.01g of carbon. Since 1 carbon atom has mass 12.01 amu, then the mass of N_A carbon atoms is $N_A \times 12.01$ amu. But 1 mole of carbon atoms has mass 12.01 g, so 12.01 g must equal $N_A \times 12.01$ amu:

$$12.01 \text{ g} = N_A \times 12.01 \text{ amu}$$

This means that

$$1 \text{ g} = N_A \text{ amu}$$

This shows that Avogadro’s number is just the conversion factor for mass between grams and amu. We didn’t randomly pick Avogadro’s number. Rather, we picked the unit of mass amu, and it turns out that there are Avogadro’s number of amu in one gram.

Review and Discussion Questions

1. State the Law of Combining Volumes and provide an example of your own construction which demonstrates this law.
2. Explain how the Law of Combining Volumes, combined with the Atomic Molecular Theory, leads directly to Avogadro's hypothesis that equal volumes of gas at equal temperatures and pressure contain equal numbers of particles.
3. Use Avogadro's hypothesis to demonstrate that oxygen gas molecules cannot be monatomic.
4. The density of water vapor at room temperature and atmospheric pressure is 0.737 g/L. Compound A is 80.0% carbon by mass, and 20.0% hydrogen. Compound B is 83.3% carbon by mass and 16.7% hydrogen. The density of gaseous Compound A is 1.227 g/L, and the density of Compound B is 2.948 g/L. Show how these data can be used to determine the molar masses of Compounds A and B, assuming that water has molecular mass 18.
5. From the results in Problem 4, determine the mass of carbon in a molecule of Compound A and in a molecule of Compound B. Explain how these results indicate that a carbon atom has atomic mass 12.
6. Explain the utility of calculating the number of moles in a sample of a substance.
7. Explain how we can conclude that 28g of nitrogen gas (N_2) contains exactly as many molecules as 32g of oxygen gas (O_2), even though we cannot possibly count this number.

By John S. Hutchinson, Rice University, 2011

Structure of an Atom

Introduction

The Atomic Molecular Theory is very powerful in helping us understand matter. We can easily understand the differences between the elements and all other compounds by thinking about the particles which make them up. Elements contain all identical atoms, and compounds contain identical molecules, each composed of definite small numbers of atoms of the elements that make up the compound. We can also do chemical algebra calculations, which allow us to make predictions about the masses of materials that are involved in chemical reactions.

Without further observations, though, this is about as far as we can go because our knowledge about the properties of atoms is very limited. We only know that atoms of different elements have different masses, and we know the relative atomic masses of the elements. But this does not give us any insight into why the atoms of different elements have such differing chemical properties. For example, carbon and nitrogen have very similar atomic masses. However, carbon in one of its forms, diamond, is a very hard, unreactive solid and in another of its solid forms, coal, carbon will burn in oxygen. Nitrogen, though, is a gas and is fairly unreactive with oxygen except at very high temperatures. Clearly, carbon atoms interact with each other very differently than nitrogen atoms interact with each other.

Without knowing anything else about atoms, we might imagine them as tiny hard spheres. But this idea will not help us understand their chemistry, such as why they form the compounds that they do. What does it mean for hydrogen and carbon to form the compound methane? We know that methane's molecular formula is CH_4 , but how do these five atoms hold together in a molecule? It seems reasonable to imagine that the attractions are due to magnetic forces or electrical forces between the atoms. However, atoms of hydrogen and carbon must be electrically neutral, since bulk samples of hydrogen and carbon are electrically neutral. They are also non-magnetic. How do neutral, non-magnetic atoms interact with each other?

Another riddle is why they form in the particular ratios that they do. CH_4 is a compound but there isn't a compound with molecular formula CH_5 .

Understanding these differing elemental and molecular properties requires us to have a deeper understanding of the properties of individual atoms. Since we cannot understand these properties by thinking of the atoms as individual hard spheres, we need to investigate the structure of the atom.

Foundation

In this study, we will assume that we know the postulates of the Atomic Molecular Theory and our measurements of relative atomic masses. We know that an element is composed of individual atoms with identical masses, and we know that the atoms of different elements have different masses, which have been measured.

We will also assume our understanding from a previous study that electricity consists of individual charged particles called electrons, which are assigned a “negative” charge. The mass of the electron is quite small relative to the mass of an atom. Atoms contain electrons, and electrons can be added to or removed from atoms by applying an electrical current.

We noted in the introduction that atoms in elemental form are neutral, or without charge. Since atoms contain negatively charged electrons, each atom must also contain a positive charge which exactly equals the total charge on the electrons in the atom. Since electrons are particles, there has to be an integer number of negative charges, so there also has to be an integer number of positive charges in each atom. These statements are important to keep in mind, but they don't help us very much without more data. We don't know how many electrons are in each atom, and therefore we don't know how many positive charges are in each atom. We do not even know whether that number of electrons is the same or different for different atoms of different elements.

In addition, we don't know how these positive and negative charges are arranged in each atom. They might be clustered together in some sort of

ball, they might be paired off together, they might be randomly arranged, or there may be some other arrangement that we don't expect.

In this concept development study, we will determine the arrangement of the charged particles in an atom, and we will determine the numbers of charged particles in the atoms of each element.

Observation 1: Scattering of α particles by atoms

To find out what the inside of an atom looks like, we perform a “scattering” experiment. This involves shooting charged particles at atoms and watching what happens. Depending on how the charged particles are arranged inside the atom, these charges should “scatter” the particles we shoot. If we look at the pattern of the scattering, we should be able to infer what the arrangement of the charges inside the atom looks like.

It would seem very hard to shoot particles at individual atoms, though, since these are very small, impossible to see, and possibly even elusive. One way to do this is to take a very thin sheet of a metal, so thin that the thickness of the metal will not be very many atoms across. Gold is a good choice of metal, since it is easy to hammer out to a very thin sheet and it is very unreactive, so it is possible to make it quite pure. In this experiment, the thickness of the gold foil will be only about 10^{-4} cm, sometimes called 1 “micron.” This is less than one-twentieth of the thickness of one human hair, so this is very thin indeed.

We need particles to shoot at this thin foil, preferably charged particles which will interact with the positive and negative charges in the gold atoms. A good choice is the α particle, which is positively charged and much more massive than an electron. In the experiment, we will fire a beam of α particles directly at the gold foil, and then we will observe where the α particles go after interacting with the gold atoms. They might pass through the foil, they might be deflected somewhat as they pass through, or they might even rebound in various angles back to the source of the beam.

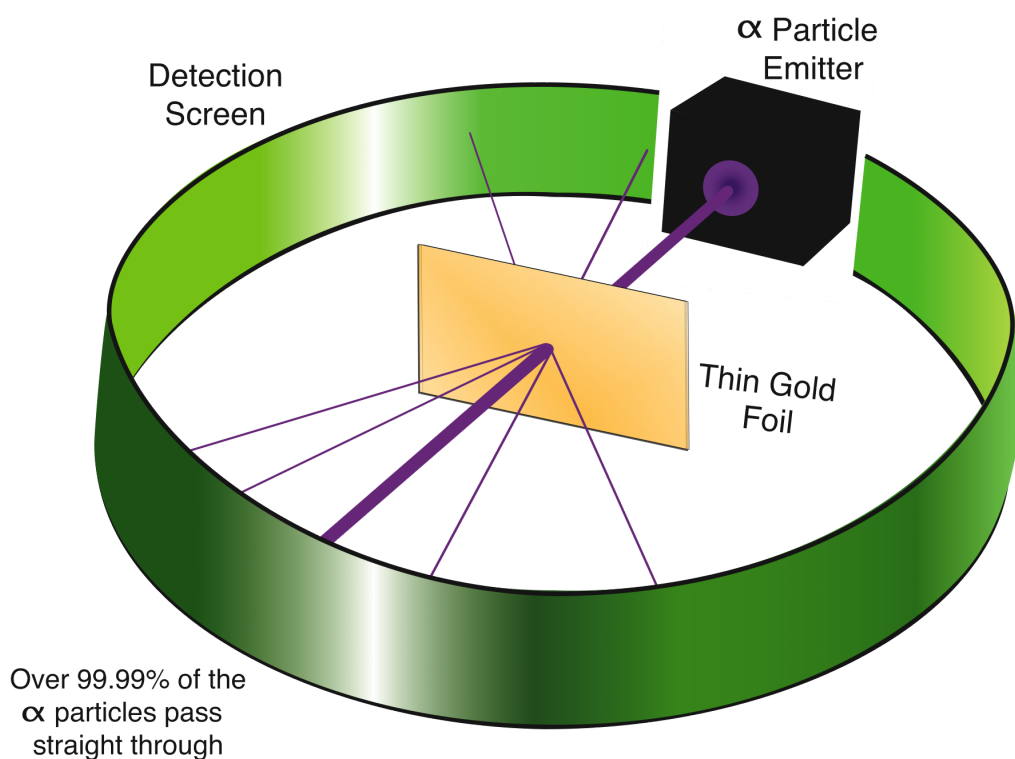


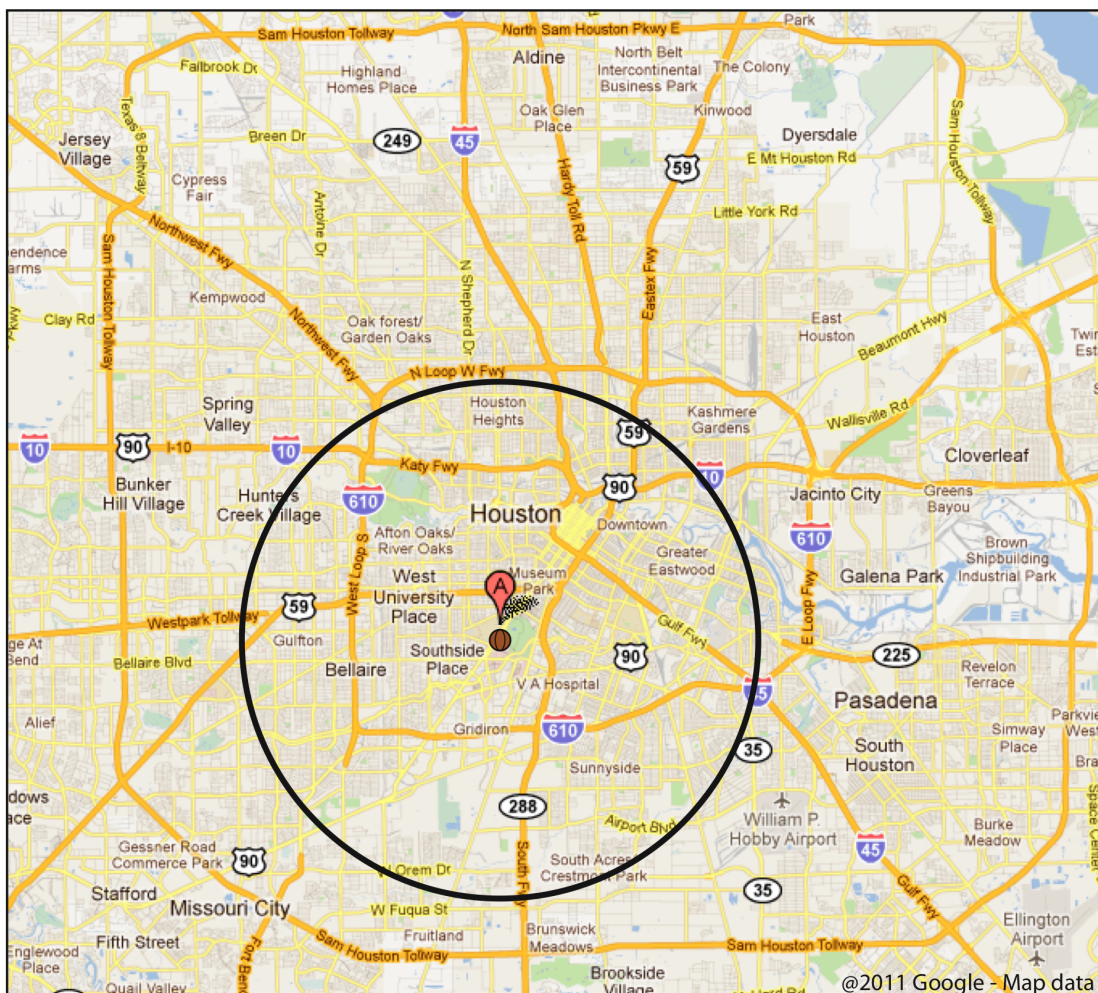
Diagram of Rutherford's gold foil experiment showing the results of shooting α particles at a very thin sheet of gold foil.

The experimental data for the scattering of the α particles shows three primary results, as depicted in [\[link\]](#). First, and perhaps most surprisingly, the greatest number of the α particles pass directly through the gold foil without any deflection in their paths. Second, a much smaller number of the α particles experience small deflections in their paths. And third, a very small fraction of the α particles (perhaps 1 in 50,000 or more) are deflected back in the direction of the beam they came from.

For now, we'll focus on the first and third observations. It is surprising that the largest number of the α particles pass through the gold foil as if it is not there. In fact, it is just as if the gold foil consisted mostly of empty space, and most of the α particles seem to pass through that empty space. This seems strange, since the gold foil is certainly solid and doesn't appear to be

empty space. The third result gives a striking contrast to this result. A tiny fraction of the α particles must encounter something other than empty space. To rebound, an α particle must hit something much more massive than itself. We might think that this is a gold atom, which is much heavier than an α particle, but to be consistent with the first observation, most of the gold atom must be empty space.

Thinking about these two observations leads us to a simple model for the atom. Each gold atom must be mostly empty space and most of the mass of the gold atom must be concentrated into a very small fraction of the volume of the atom. We will call this concentrated mass the “nucleus.” A careful calculation based on the fraction of α particles which pass through and the fraction which rebound tells us that the diameter of the nucleus is about 100,000 times smaller than the diameter of the atom itself. This is an amazing result! Although an atom is very small, the nucleus is very much smaller than that, as analogously depicted in the diagram in [\[link\]](#).



This map illustrates the size of an atom if the nucleus were a standard-sized basketball at Lovett Hall on the Rice University campus. The atom is 100,000 times large than the nucleus, so on this map this model of an atom has a radius of 11.9 km.

This is an interesting model that seems to account for two of our three observations, but it is a puzzling model too. If the mass of the atom is concentrated in such a small space, what occupies the rest of the volume of the atom? The second observation from the experiment helps us understand this. Since a small number of the positively charged α particles are deflected in their paths, this suggests that they come close to but do not run into something positive in the atom. Since these α particles are deflected,

whatever they come close to must be more massive than they are. This means that they are coming close to the nucleus and the nucleus must be positively charged.

This gives us a clue about what occupies the vast empty space of the atom. If the positive charges of the atom are concentrated in the nucleus, the negative charges in the atom, the electrons, must be in the much larger space of the atom outside of the nucleus. This nuclear model of the atom then accounts for all three observations in the α particles gold foil scattering experiment. Most of the volume of the atom is empty space in which negatively charged electrons move about. Most of the mass and all of the positive charge of the atom is concentrated in a nucleus, which is tiny in comparison to the atom.

Observation 2: X-ray emissions from atoms

It is interesting to know that each atom has a nuclear structure, particularly since we now know that the positive and negative charges in the atom are separated into different parts of the atom. The interaction of these positive and negative charges must be what determines the properties of each type of atom, including the types of molecules that they tend to form. Even though each atom is neutral, it might be possible for the positive charges on one atom to interact with the negative charges on another atom, and vice versa. To show this, we would need to know how many positive and negative charges there are in each atom. It seems reasonable to assume that these numbers are different for atoms of different elements, but we don't know that without making more observations.

At this point, we know that atoms contain electrons, and that there are an integer number of these. We also know that each atom contains an equal number of positive charges, all of which are in the nucleus. It makes sense that, since the positive charge is an integer, there must be particles of positive charge in the nucleus, and we will now call these particles "protons." This doesn't make our life any easier, but it does clarify our language.

Our problem now boils down to finding out how many protons and how many electrons there are in each atom of each type. These integers are the same number for each atom, of course, since each atom is neutral. Finding this integer for each element seems quite difficult, and the experiment which reveals the number to us is a strange one which doesn't seem related to the question at all.

When materials are placed in an electrical discharge, they commonly emit light or "electromagnetic radiation." Not all of this light is visible. Some of this light is high-energy light called ultraviolet radiation, and some of it is even higher energy radiation called x-rays. We can tell the difference between different types of radiation by the "frequency" of the radiation, a property that tells us how rapidly the electromagnetic field of the radiation oscillates. Different frequencies of radiation can be separated by passing the radiation through different materials. This is how a prism works, for example. We can also separate the different frequencies with something called a "diffraction grating," which can be either a solid with parallel grooves or a transparent solid with closely spaced lines. As common examples of simple diffraction gratings, compact discs and DVDs have grooves in parallel to each other and can be used to produce a visible rainbow. A white light source will reveal the different colors of light, each with its own frequency, when the light is reflected off of the surface of the disc.

This separation of light into different frequencies is very useful in a type of experiment called "spectroscopy." There are many types of spectroscopy, but in most cases, a sample of a material is energized in some way, often in an electrical discharge, and the sample emits light. This is an everyday observation. For example, heated objects tend to glow, which means that they are emitting light. In spectroscopy, the light which the sample emits is separated by a prism or a grating and a wonderful result occurs. Each different element or compound has its own characteristic set of frequencies of light which are emitted. In other words, only certain frequencies of light are emitted by each substance, and the set of frequencies for each substance is unique to that substance. Spectroscopy has great value in science, because we can identify that a sample contains a particular compound or

element just by looking at the frequencies of light that the sample emits. This is how we know the composition of distant stars, for example.

We need to focus on atoms, so we'll look only at the spectroscopy of pure elements. Each element has a characteristic spectrum of frequencies. We will focus on the light frequencies which are x-rays and, even more carefully, for each element we will focus on the lowest frequency x-ray which each atom emits. These are given for many of the elements in [\[link\]](#). The ordering of the elements in [\[link\]](#) is important. We could have listed them alphabetically by name. Instead, we have listed them in their order of increasing relative mass. In the set of elements given here, lithium is the least massive element so it is at the top, then beryllium, and so forth. Note that the x-ray frequency emitted by each atom increases as the masses of the atoms increase moving down [\[link\]](#). (There is one exception to our order in [\[link\]](#): Argon is slightly more massive than Potassium, but we have put Argon before Potassium for reasons that we will discuss later.)

Atomic Number	Element Name	X-ray frequency (10^{16} s^{-1})
3	Lithium	1.3158
4	Beryllium	2.6316
5	Boron	4.4379
6	Carbon	6.7114
7	Nitrogen	9.4937
8	Oxygen	12.701

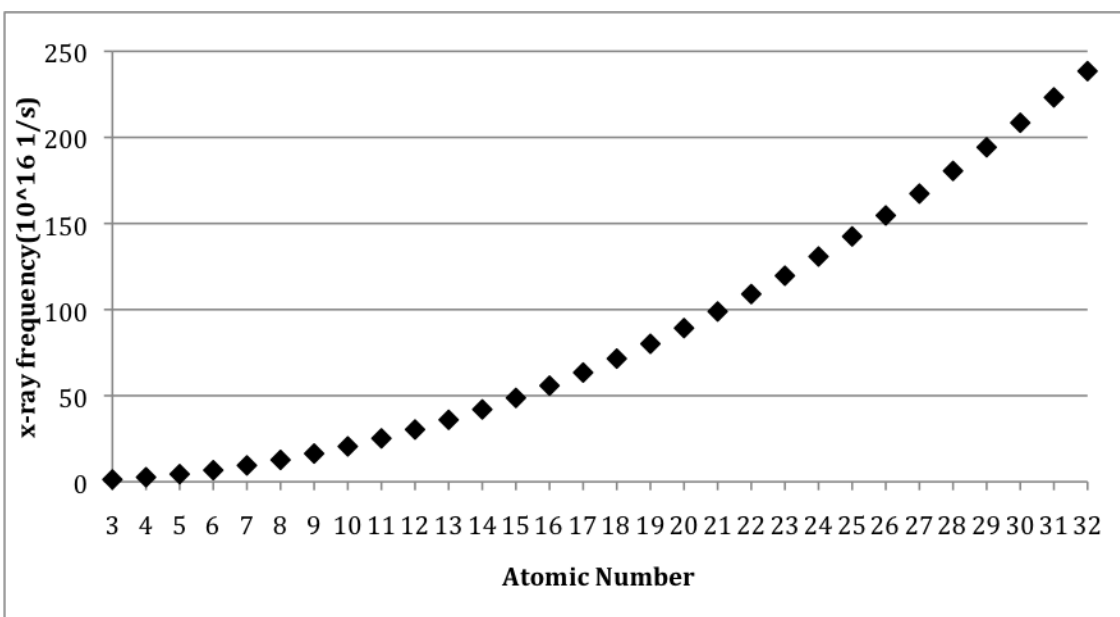
Atomic Number	Element Name	X-ray frequency (10^{16} s^{-1})
9	Fluorine	16.376
10	Neon	20.534
11	Sodium	25.189
12	Magnesium	30.334
13	Aluminum	35.971
14	Silicon	42.008
15	Phosphorous	48.701
16	Sulfur	55.814
17	Chlorine	63.416
18	Argon	71.518
19	Potassium	80.118
20	Calcium	89.242
21	Scandium	98.873
22	Titanium	109.01
23	Vanadium	119.65
24	Chromium	130.80
25	Manganese	142.47

Atomic Number	Element Name	X-ray frequency (10^{16} s^{-1})
26	Iron	154.65
27	Cobalt	167.33
28	Nickel	180.53
29	Copper	194.25
30	Zinc	208.48
31	Gallium	223.21
32	Germanium	238.47

X-ray Frequencies of Atoms

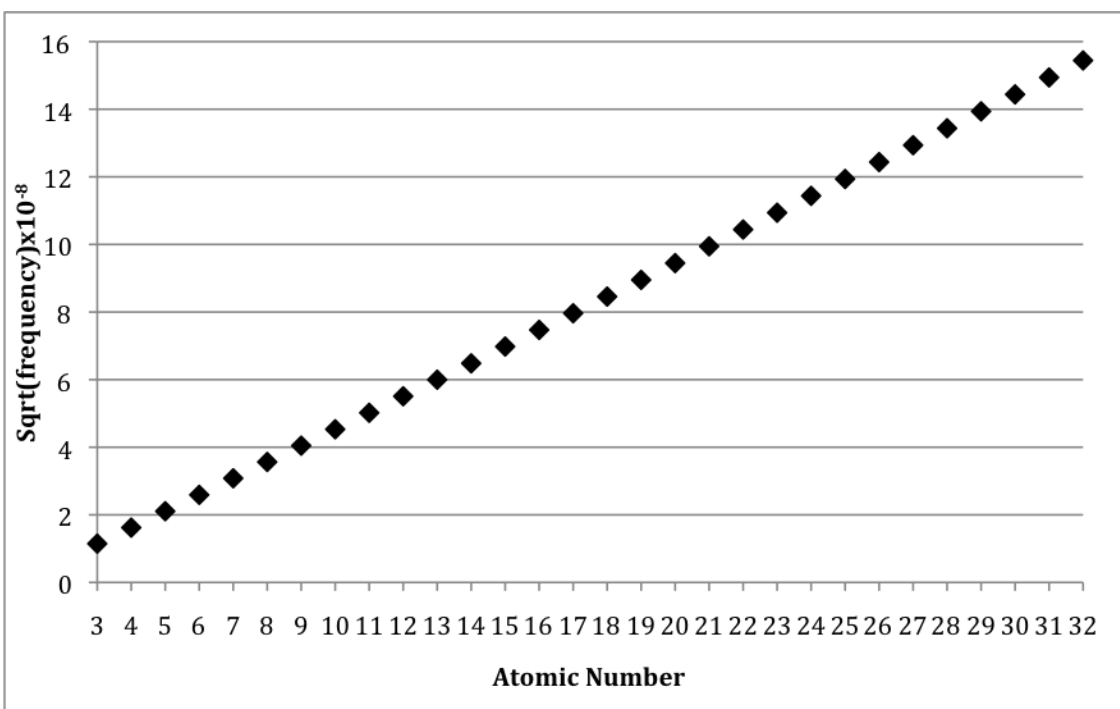
We have also added something interesting in [\[link\]](#), the “atomic number.” This number is just the ranking of the elements in order of increasing mass. The atomic number then is just another name we have given to each element with no more significance than the names we have given. (Note again that Argon is placed before Potassium. There are other reasons for this, but this also makes sense in the data, since this way, the frequencies of the x-rays increase.)

Other than the fact that the x-ray frequencies consistently increase, there doesn't seem to be any other obvious pattern in the data. We could look for a pattern by plotting the x-ray frequency versus the masses of the atoms, but this doesn't show anything additional. Surprisingly, though, if we plot the x-ray frequency versus the atomic number, a clear pattern emerges, as we see in [\[link\]](#).



X-ray frequency vs. atomic number for the elements lithium to germanium.

The frequencies don't just increase with atomic number, they increase with a very smooth function. This type of graph might look familiar to you. It looks similar to a graph of $y = x^2$, called a parabola. Is the graph in [\[link\]](#) a parabola? To find out, we need to know whether the x-ray frequency is a function of the atomic number squared. One way to do this is to plot the square root of the x-ray frequency versus the atomic number. This would be like plotting the square root of y versus x to see if $y = x^2$. This new graph is shown in [\[link\]](#).



The square root of x-ray frequencies vs. atomic number for the elements lithium to germanium.

The graph in [\[link\]](#) is very significant. It shows that there is a simple relationship between the x-ray frequency emitted by each atom and the atomic number of the atom. But this is a strange result. The x-ray frequency is a physical property of each atom. The atomic number is just an integer that we assigned to each element based on its mass ranking. This is a surprise! Why would a physical property match up so strongly with a non-physical property like an integer in the mass rankings? There is only one possibility: the atomic number must also be a physical property of the atom. It is not an arbitrary number, even though we assigned it that way initially. It is a property of the atom.

The atomic number is also a special property of the atom because it is an integer, and integers are used to count objects or particles. This means that the atomic number must be counting some integer number of objects or particles in each atom, and that number must be unique for each atom. But

we know that there is an integer that describes each atom: the number of protons and electrons that each atom has.

Our conclusion is therefore that the atomic number is a property of each atom which is equal to the number of protons in each atom and is also equal to the number of electrons in each atom. We have found a way to count the number of charges in each atom! There are two remarkable results to mention here. The first is that each atom has its own characteristic number of protons and electrons. This is not shared with any other atom. This suggests that these numbers must be important in determining the chemical and physical properties of the atom. The second is that every integer number of protons and electrons is accounted for. There are no gaps or breaks in [\[link\]](#) or in [\[link\]](#) or [\[link\]](#). We have them all. There are no missing elements in the range from 3 to 32, nor for that matter from 1 to 114. This is why there are only a small number of elements (about 90 naturally occurring ones).

We now know what is unique about the atoms of different elements. It does make sense that atoms with different numbers of charged particles would interact differently, forming compounds with different chemical and physical properties. But we might imagine that atoms with similar (but not equal) numbers of charged particles would have fairly similar chemical and physical properties. As we will explore in much more detail later, this is not at all the case. In fact, it is possible to compare two elements with very similar atomic numbers, say Neon and Sodium, and find that their chemical properties are completely different. Neon is a gas, even at extremely low temperatures, and is so unreactive that it does not form compounds with any other elements. Sodium is a solid which is so reactive that its reactions with other elements are often violent and energetic. It seems clear that just knowing how many electrons an atom has is not sufficient to make predictions about how that atom might behave. We will need to refine our model with further observations.

Review and Discussion Questions

1. Explain how the scattering of α particles from gold foil reveals that an atom contains a massive, positively charged nucleus whose size is

much smaller than that of an atom.

2. Explain the significance of the relationship between the frequency of x-ray emission from each atom and the atomic ranking of that atom in the periodic table.

By John S. Hutchinson, Rice University, 2011

Electron Shell Model of an Atom

Introduction

What more could we want to know about the structure of an atom? We know that atoms contain positively and negatively charged particles, and that the number of these charges in each atom is different for each element. We also know that the positive charges are concentrated in a tiny nucleus, and that the electrons move around the nucleus in a space that is much, much larger than the nucleus.

However, some of the most important questions we asked in the previous Concept Development Study are still unanswered. Remember that we saw that carbon and nitrogen have very similar atomic masses. Now we can add that these elements have very similar atomic numbers, so their atoms have similar numbers of protons and electrons. But carbon and nitrogen are, in most chemical and physical ways, very different. Similarly, some elements like sodium and potassium have very different atomic numbers but have quite similar chemical and physical properties. It seems that comparing the properties of two different atoms is not very easy to understand just from comparing the numbers of protons and electrons the atoms contain.

To continue to understand the answers to these questions, we need even more detail about the structure of each type of atom.

Foundation

In this study, we will assume that we know the postulates of the Atomic Molecular Theory and our measurements of relative atomic masses. We know that an element is composed of individual atoms with identical masses, and we know that the atoms of different elements have different masses, which have been measured.

We will also assume that we know that structure of an atom, with a tiny, massive, positively charged nucleus surrounded by a much larger empty space in which electrons move. The positive charge on the nucleus is equal to the number of protons in the nucleus and, in a neutral atom, is also equal to the number of electrons moving about the nucleus. The number, called the atomic number, is unique for each type of atom. No two elements have the same atomic number, and amongst the naturally occurring elements, no atomic number is skipped: for every integer up to 118 we know an element with that atomic number.

In this study, we will need a very important observation borrowed from the study of Physics. We will use Coulomb's Law to describe the interaction of charged particles. Coulomb's Law is an algebraic expression which relates the strength of the interaction between two charged particles to the sizes of the charges on the particles and the distance between them. We can think of the strength of the interaction between particles as either the force that one particle exerts on the other particle or the potential energy which exists when the two particles interact with each other. We will focus on the potential energy, which we will call V . Let's think of two particles, one with charge q_1 and the other with charge q_2 . These charges can be either positive or negative, depending on the properties of the particles. Let's place the two particles a distance r away from each other. Then the potential energy of interaction between these two charged particles is:

$$V = \frac{(q_1)(q_2)}{r}$$

This is Coulomb's Law. We will very rarely do any calculations with this equation. Instead, we will apply it to understand when V is expected to be a large number or a small number, positive or negative. When V is a large negative number, the potential energy is very low and the two charges are strongly attracted to one another. To see this, think about what must happen to pull two charges apart which have a very negative potential energy. If we want r to become very large, then in Coulomb's Law, we want V to get close to zero. If V is a large negative number, then we have to add a lot of energy to bring V up to zero. Therefore, a large negative value of V means that the two particles are strongly attracted to each other since it requires a lot of work to pull them apart.

In the equation above, V will be a large negative number when several things are true: the charges must have opposite signs, so that multiplying them together gives a negative number. All this means is that opposite charges attract. The larger the charges, the stronger the attraction. In addition, r must not be large and preferably will be fairly small. These simple conclusions must be kept in mind. Two particles with large opposite charges close to one another must be strongly attracted to one another. The smaller the charges or the larger the distance, the weaker the attraction.

In many ways, it is fair to say that Coulomb's Law forms the foundation of everything we know about the chemistry of atoms and molecules. Therefore, it is very important to understand the conclusions of the previous paragraph. Without them, we can make no further progress in our understanding of atoms.

Observation 1: Periodic Properties of the Elements

We now have much more information about the differences between the atoms of different elements. We know how many electrons and protons each atom contains, and we know where these charged particles are in the atom, with the protons in a very small nucleus and the electrons occupying the vast empty space around the nucleus. It seems that we should be able to account for the chemical properties of these atoms by using this information. However, we rapidly run into a surprising result.

Remember that the atomic number tells us how many protons and electrons an atom contains. We observe that atoms with very similar atomic numbers often have very different chemical properties. For example, carbon's atomic number is 6 and nitrogen's is 7, so they have very similar numbers of protons and electrons. But as we have seen, elemental carbon is a solid and elemental nitrogen is a gas. Oxygen's atomic number is 8, just one greater than nitrogen, but oxygen reacts with most other elements, sometimes violently, whereas nitrogen is so unreactive that it is often used to provide an "inert" atmosphere to store chemicals.

Also surprisingly, elements with very different atomic numbers can have quite similar chemical properties. The elements fluorine and chlorine are both gases and both exist as diatomic molecules in nature, F_2 and Cl_2 . Both are highly reactive and will combine with hydrogen to form acids, HCl and HF . They both combine with metals like sodium and magnesium to form solid salts with similar molecular formulas, like NaF and $NaCl$. But their atomic numbers are quite different: F 's atomic number is 9, and Cl 's is 17.

It should seem strange that elements with very different numbers of charged particles should behave alike chemically, but elements with very similar numbers of charged particles should behave very differently chemically. There must be more to learn about what determines the chemistry of individual atoms.

One clue is found in looking at the pattern of elements which have similar chemical properties. We can go to [\[link\]](#), which lists the elements by relative atomic mass and, as we now know, by atomic number. Let's pick out three elements with similar properties: lithium, sodium, and potassium. All three of these elements are soft metals with low melting points, all three react violently with water, and all three form salts with chlorine with the similar molecular formula, LiCl, NaCl, KCl. Because these elements are so similar, they can be regarded as a "group," and a name has been given to this group, the "alkali metals." Surprisingly, immediately before each of these elements in the list are three elements which are also very similar to each other but very different from the alkali metals. These are the "noble gases," helium, neon, and argon. These elements are all gases to very, very low temperatures, and they are all very unreactive, sometimes called "inert." The fact that each alkali metal is always preceded by a noble gas suggests that there is a pattern to the properties of the elements.

We can see this again by looking at the elements immediately after each alkali metal. These are beryllium, magnesium, and calcium, and again these three have very similar properties. They are all soft metals with higher melting points than the alkali metals, and they all form salts with chlorine with similar molecular formulas, BeCl₂, MgCl₂, and CaCl₂. Because they are similar, we place them in a group together, which has been called the "alkaline earth metals."

In fact, we can keep this up with other groups. The elements that are just before the noble gases are fluorine and chlorine, which again have very similar chemical properties as we discussed before. Later on in the list of elements, the noble gas krypton is immediately preceded by the element bromine, which also has similar properties to chlorine and fluorine. We place fluorine, chlorine, and bromine in a group together called the "halogens."

Atomic Number	Element Name	Element Symbol	Relative Atomic Mass
1	Hydrogen	H	1.0079
2	Helium	He	4.0026
3	Lithium	Li	6.941
4	Beryllium	Be	9.0122
5	Boron	B	10.811
6	Carbon	C	12.011
7	Nitrogen	N	14.007
8	Oxygen	O	15.999
9	Fluorine	F	18.998

10	Neon	Ne	20.180
11	Sodium	Na	22.990
12	Magnesium	Mg	24.305
13	Aluminum	Al	26.982
14	Silicon	Si	28.086
15	Phosphorous	P	30.974
16	Sulfur	S	32.066
17	Chlorine	Cl	35.453
18	Argon	Ar	39.948
19	Potassium	K	39.098
20	Calcium	Ca	40.078
21	Scandium	Sc	44.956
22	Titanium	Ti	47.876
23	Vanadium	V	50.942
24	Chromium	Cr	51.996
25	Manganese	Mn	54.938
26	Iron	Fe	55.845
27	Cobalt	Co	58.933
28	Nickel	Ni	58.693
29	Copper	Cu	63.546
30	Zinc	Zn	65.39
31	Gallium	Ga	69.723
32	Germanium	Ge	72.61
33	Arsenic	As	74.922
34	Selenium	Se	78.96

35	Bromine	Br	79.904
36	Krypton	Kr	83.80

Atomic Number and Relative Atomic Mass of Elements

The striking observation is that the groups of elements appear “periodically” in the ranking of the elements by atomic number. Looking at the list in [\[link\]](#), in each case we find, in order, a halogen, a noble gas, an alkali metal, and an alkaline earth metal, and this pattern repeats itself over and over again. This observation is called the Periodic Law, and it is the reason that the usual table of the elements is called the “Periodic Table,” which is arranged with the elements in each group placed together in columns.

Periodic Law: The chemical and physical properties of the elements are periodic functions of the atomic number.

This observation is very surprising! To see this, consider an analogy. Imagine we looked for a pattern in the grades of students in a class by where they like to sit. We would not be surprised to find a pattern. Perhaps, for example, the most attentive students sit in a group near the front of the class and make the highest grades. However, we would be very surprised if we were to rank the students in order of decreasing grades and discover that every tenth student (1st, 10th, 21st, 31st) in the list sat in the first row, every other tenth student (2nd, 12th, 22nd, 32nd) sat in the second row, and so forth. That would be very unexpected and very hard to explain. But we would look for a reason for the pattern. In a similar way, we have seen a surprising pattern in the behavior of the elements with atomic number, and we must look for a reason for that pattern.

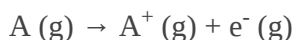
Observation 2: Ionization Energies of the Atom

We are now ready to use Coulomb’s Law, as discussed in the Foundation, to understand the attraction of the electrons flying about the nucleus to the positive charge of the nucleus. Recall that the attraction of two charges together depends on the sizes of the charges and the distance between them. The size of the charge on an electron is often called $-e$. In the case of an atom with atomic number Z , there are Z protons so the nuclear charge is $+Ze$. The attraction of an electron at distance r away from this nucleus is given by the potential energy in Coulomb’s Law:

$$V(r) = \frac{(+Ze)(-e)}{r}$$

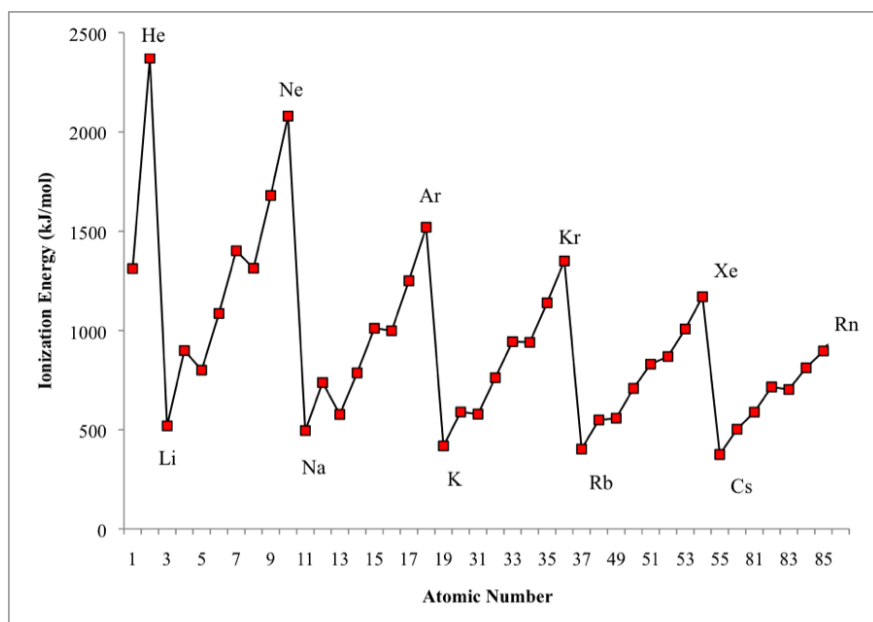
This means that an electron close to the nucleus would be more strongly attracted to the nucleus, because its potential energy is much more negative. A large negative potential energy means that we would have to add a lot of energy to the electron to remove it from the atom so that r could become large. This also means that an electron in an atom with a large atomic number, Z , would be more strongly attracted to its nucleus than an electron in another atom with a smaller atomic number.

We can actually observe the attractions of the electrons to the nucleus by measuring the amount of energy required to remove the electron from the atom. This energy is called the “ionization energy” of the atom because it is the energy required to take a neutral atom and turn it into a charged ion:



In this chemical process, A is an atom, the (g) means that this atom is in the gas phase, and $A^+(g)$ is the same atom with one electron removed, leaving behind a positive charge. We call A^+ an ion. Think about how the ionization energy is related to the potential energy in Coulomb's Law. For an electron to be removed from the atom, r must become very large so that the potential energy becomes essentially zero. If an electron began with a negative potential energy $V(r)$, we would have added at least this much energy to bring the potential energy up to zero. Therefore, a large negative $V(r)$ would require a large ionization energy. We often call the ionization energy, IE, and it is typically measured in kilojoules (kJ) per mole of atoms. At this point, we don't need to worry about how this experiment is actually done.

The experimental data found from measuring the ionization energies of the elements are shown in the graph in [\[link\]](#).



Ionization energy of the main group elements by atomic number.

The first thing to notice in [\[link\]](#) is that the Periodic Law definitely applies to this particular property of the atoms. As we look at the atoms with increasing atomic number, the ionization energies increase and then abruptly decrease, over and over. At the top of each peak sits a noble gas element. At the bottom of each valley sits an alkali metal. Between each alkali metal and the next noble gas, the ionization energies increase almost continuously, with only small breaks along the way. This is a great confirmation of the Periodic Law.

In this case, we can actually start to understand the patterns in [\[link\]](#) from thinking about Coulomb's Law. The easiest property to understand is that in each period in the figure, the ionization energy increases as we move from an alkali metal (like Li) to the next noble gas (like Ne). This makes sense in terms of Coulomb's Law, because the atomic number, Z , is increasing, so the nuclear charge is increasing, so the electrons are more strongly attracted to the nucleus as Z increases.

If we follow this line of thinking, we might expect that the ionization energies would just constantly increase with increasing atomic number Z . But this is not observed. Instead, after each noble gas, the ionization energy drops very dramatically to the following alkali metal (as in going from Ne to Na). Looking at the equation for Coulomb's Law, how can it be that a larger value of Z from Na compared to Ne can result in a much, much smaller ionization energy?

The answer is in the denominator of Coulomb's Law, the distance r . The only way for the ionization energy to get smaller when Z gets larger is for r to get larger as well. In fact, r has to get much larger since the ionization energy falls by such a large amount. This means that the electron which is ionized in Na is much farther from the Na nucleus than the electron in Ne which is ionized is from the Ne nucleus.

Perhaps this means that r just increases smoothly as the atomic number gets larger. But the data do not show this at all. After Na, the ionization energies of the atoms continue to grow again with the increasing atomic number, Z , and the larger charge of the nucleus.

Putting these two conclusions together, we can create a model of the atom that explains the Periodic Law and the Ionization Energies in [\[link\]](#). In each period of the Periodic Table from an alkali metal to a noble gas, the outermost electrons are all about the same distance from the nucleus. Each additional electron in each atom in one period is added to this same "layer" of electrons, which we will call an "electron shell." At the end of the period, the shell is apparently full and unable to accommodate any more electrons. The next added electron in the next period must be in a new shell, much farther from the nucleus.

It is worth reviewing how this "shell" model of the atom's structure explains the pattern in the ionization energies in [\[link\]](#). This is left as a discussion question. Beyond that, though, there is an explanation for the Periodic Law. Why, for example, do the alkali metals Li, Na, and K, have such similar properties? The answer from our shell model is that each of these atoms has a single electron in its outermost shell, even though they have very different numbers of electrons in total. That outermost electron is the one which must determine the chemical behavior of the atom. Similarly, F and Cl have very similar chemical properties because, from the data in [\[link\]](#), we can tell that each of these types of atoms have 7 electrons in the outermost shell. Again, the number of electrons in the outermost shell of the atom appears to determine the atom's chemical and physical properties.

Because this outermost shell is the most important shell, it is given the name "valence shell," and the electrons in that shell are called "valence electrons." The word "valence" means "importance." The valence electrons are the most important electrons in each atom.

Observation 3: Successive Ionization Energies of the Atom

There is another more direct way for us to observe the number of valence electrons in each atom and to show that they are all in about the same shell. We can attempt to remove each electron in the valence shell, one after the other, increasing the charge on the ion to higher and higher values. We have discussed the first ionization energy, which is the energy to remove one electron. The second ionization energy is the energy needed to remove an electron from the positive ion to form an ion with a +2 charge. There are also third and fourth ionization energies and beyond:

First ionization energy $IE_1 \text{ A (g)} \rightarrow \text{A}^+ \text{ (g)} + \text{e}^- \text{ (g)}$

Second ionization energy $IE_2 \text{ A}^+ \text{ (g)} \rightarrow \text{A}^{2+} \text{ (g)} + \text{e}^- \text{ (g)}$

Third ionization energy $\text{IE}_3 \text{ A}^{2+}(\text{g}) \rightarrow \text{A}^{3+}(\text{g}) + \text{e}^{-}(\text{g})$

Fourth ionization energy $\text{IE}_4 \text{ A}^{3+}(\text{g}) \rightarrow \text{A}^{4+}(\text{g}) + \text{e}^{-}(\text{g})$

The experimental data observed when doing these “successive” ionizations is shown in [\[link\]](#):

	Na	Mg	Al	Si	P	S	Cl	Ar
IE_1	496	738	578	787	1012	1000	1251	1520
IE_2	4562	1451	1817	1577	1903	2251	2297	2665
IE_3	6912	7733	2745	3231	2912	3361	3822	3931
IE_4	9543	10540	11575	4356	4956	4564	5158	5770
IE_5	13353	13630	14830	16091	6273	7013	6542	7238
IE_6	16610	17995	18376	19784	22233	8495	9458	8781
IE_7	20114	21703	23293	23783	25397	27106	11020	11995

Successive Ionization Energies of the Atoms (kJ/mol)

Let's analyze this data, looking for evidence of the valence shell and the number of valence electrons. First, for every atom listed, IE_2 is always greater than IE_1 , IE_3 is greater than IE_2 , and so forth. This makes sense when we remember that the negatively charged electrons in an atom repel one another. Once an electron has been removed from an atom, the remaining electrons will have lower energy and be harder to remove.

Looking more closely, though, the increases in the ionization energies are not very constant. In Na, IE_2 is greater than IE_1 by a factor of almost nine, but IE_3 is greater than IE_2 by a fraction, and the same is true with the higher ionization energies. This means that the first electron in Na is fairly easy to remove, but the second one is much harder. This means that the first electron removed from Na is in the valence shell, far from the nucleus, but the second electron removed is closer in and more strongly attracted. The third electron removed is harder still to remove, but not much. This means that the third electron removed is in the same shell as the second one. Therefore, Na has only one valence electron.

Now look at Mg. The first electron doesn't require much energy to remove, although it is more than in Na. The second electron is harder again, but the real change is when we try to remove the third electron. Suddenly we see an increase of a factor of 5 in the ionization energy. This means that Mg has two relatively easily removed electrons, and therefore Mg has two valence electrons. Looking at the data in [\[link\]](#), we can simply count the number of valence electrons in each atom. (It is hard to do this for Cl and Ar, because it is hard to remove this many electrons from a single atom.)

The shell model of the atom tells us how the electrons are arranged in each atom, but it does not tell us why. We don't know why the electrons can't all be added to a single shell, because we don't know why a shell seems to "fill up." It is clear from the data that the number of valence electrons in each noble gas is the number needed to fill the valence shell. But we don't have a reason why this is true. These questions will require further observations and reasoning.

Review and Discussion Questions

1. Provide the experimental evidence that reveals the electrons in an atom are grouped into a valence shell and inner shell electrons.
2. State and explain the evidence that reveals the outer shell of each inert gas is full.
3. Why does the ionization energy for each successive ionization increase for every atom? Why is the increase from IE_4 to IE_5 in Si much larger than any of the other increases for Si?

By John S. Hutchinson, Rice University, 2011

Quantum Electron Energy Levels in an Atom

Introduction

The electron shell model for the atom provides significant answers to many of the most important questions about the properties of atoms. For many of the problems that chemists need to solve, we don't need more details about the structure of the atom than what we can gain from knowing the numbers of electrons in the valence shell, the size of the valence shell, and the charge on the nucleus. As perhaps the best example of this, the Periodic Law of the elements is easily understood from the repeating pattern of filling a valence shell successively and starting over with a new shell. Even though more advanced and detailed theories of atomic structure have come along since the electron shell model was introduced, chemists return to this simple model to understand the properties of elements and the structures and reactions of molecules. We shall come back and explore these applications of the electron shell model in later Concept Development Studies.

For now, there are still some nagging questions about this simple model. What does it mean for two or more electrons in an atom to be "in the same shell"? We don't have a model for what a shell is, other than a set of electrons which appear to be at about the same distance from the nucleus. But this does not give a clear picture of what the electrons are doing. We have said that the electrons move in the empty space surrounding the nucleus, but we have not yet asked how they move or where they move. Without knowing that, we cannot really know why electrons have similar or different energies.

Probably the most important unanswered question is why the shells fill up. The arrangement of elements into groups and the periodicity of chemical properties both depend on the idea that a shell is "filled" by a certain number of electrons. Why is there a limit on the number of electrons which can "fit" into a shell? Looking at the number of elements in each period, the number of electrons which fills a shell depends on which shell is being filled. There are 8 elements from lithium to neon and from sodium to argon, telling us that 8 electrons will fill the valence shells in each of those sets of elements. However, there are 18 elements from potassium to krypton and

from rubidium to xenon, telling us that 18 electrons will fill the valence shells in each of those sets of elements. In the cases of hydrogen and helium, only 2 electrons will fill their shell. What determines how many electrons can “fit” in a shell? What is special about the numbers 2, 8, and 18? Why is there a limit at all? These may seem like questions about only technical details. But the power of the electron shell model rests on these details, so we should find out the answers to these questions.

Foundation

In this study, we will assume that we know the postulates of the Atomic Molecular Theory and our measurements of relative atomic masses. We know that an element is composed of individual atoms with identical masses, and we know that the atoms of different elements have different masses, which have been measured.

We will also assume that we know the structure of an atom, with a tiny, massive, positively charged nucleus surrounded by a much larger empty space in which electrons move. The positive charge on the nucleus is equal to the number of protons in the nucleus and, in a neutral atom, is also equal to the number of electrons moving about the nucleus. The number, called the atomic number, is unique for each type of atom. No two elements have the same atomic number, and amongst the naturally occurring elements, no atomic number is skipped: for every integer up to 118 we know an element with that atomic number. We will assume knowledge of the concept of electron shells as a means of understanding the Periodic Law, which describes the chemical and physical properties of the elements.

From the previous Concept Development Studies, we shall also assume an understanding of Coulomb’s Law to describe the interactions of the protons and electrons in an atom. And we shall also assume an understanding that light, or electromagnetic radiation, can be described in terms of the frequency of the light and that the frequencies emitted by a light source can be separated by using a prism or diffraction grating. We will use each of these understandings as we probe into greater detail about the structures of atoms.

Observation 1: The Spectrum of Hydrogen

In the Concept Development Study on Atomic Structure, we discussed the experimental method called “spectroscopy.” In general in a spectroscopy experiment, we look at the frequencies of light that an atom or molecule emits when energy is added to it in some way (commonly by heating it or placing it in an electric arc but possibly also by shining light on it).

Alternatively, we can also look at the frequencies of light which the atom or molecule absorbs when we shine light with a range of frequencies on the atom or molecule. These two techniques are called “emission spectroscopy” and “absorption spectroscopy,” and which method is used depends on what properties we are trying to measure.

In the simple case of an atom, say hydrogen, the frequencies of light which the atom will absorb are the same as the frequencies of light which the atom will emit. We can look at either one, and the set of frequencies we see experimentally is called the “spectrum” of the atom. Since hydrogen is the simplest atom, with only a single proton and a single electron, we’ll look at hydrogen’s spectrum first.

The spectrum of hydrogen contains frequencies of light corresponding to visible light, ultraviolet light, and x-rays. The visible spectrum of hydrogen, which is just the four frequencies hydrogen emits that can be seen by the human eye, is shown in [\[link\]](#). There are many more frequencies in hydrogen’s spectrum than the ones that we can see. [\[link\]](#) shows a set of these frequencies.

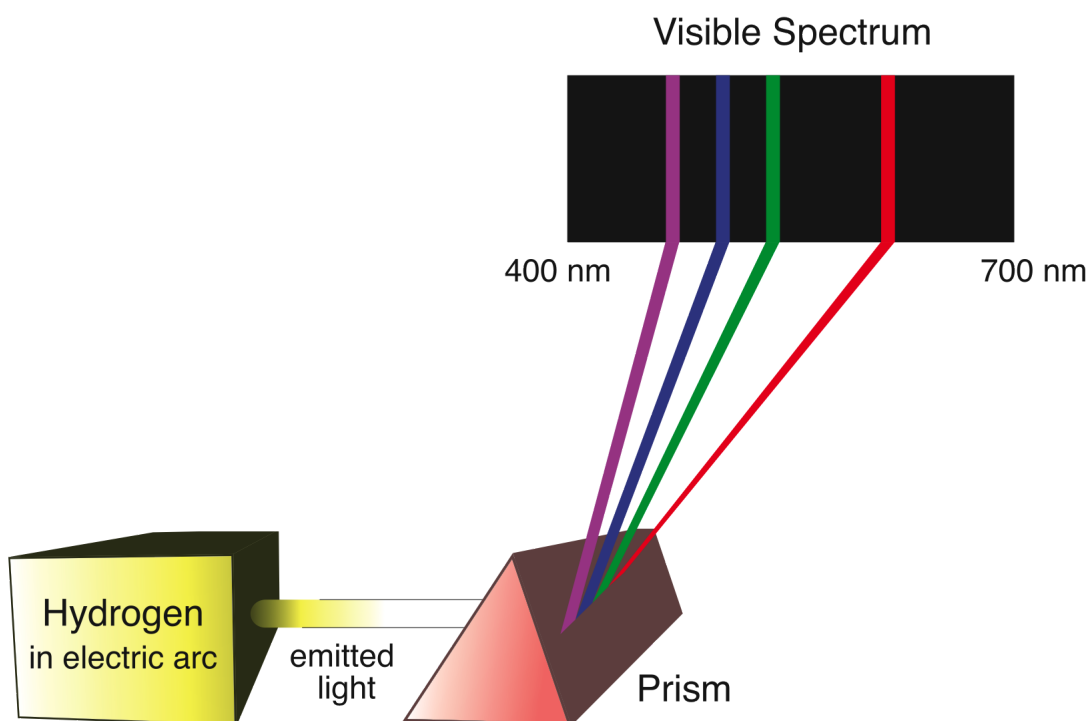


Diagram showing the visible emission spectrum of hydrogen corresponding to light at 410, 434, 486, and 656 nm wavelengths.

Wavelength (nm)	Frequency (THz)	Region(color)
94	3197	Ultraviolet
95	3157	Ultraviolet
97	3083	Ultraviolet

103	2922	Ultraviolet
122	2466	Ultraviolet
410	731	Visible (violet)
434	691	Visible (violet-blue)
486	617	Visible (blue-green)
656	457	Visible (red)
955	314	Infrared
1005	298	Infrared
1094	274	Infrared
1282	234	Infrared
1875	160	Infrared

Hydrogen Spectrum

There doesn't appear to be a pattern of any sort in the data in [\[link\]](#), just a collection of numbers. The first important conclusion to remember, though, is that only these frequencies are observed. Hydrogen atoms will not emit radiation with a frequency between these numbers, for example. Given the infinite possibilities for what the frequency of light can be, this is a very small set of numbers observed in the spectroscopy experiment.

As it turns out, there is a pattern in the data, but it is quite hard to see. Each frequency in the spectrum can be predicted by a very simple formula, in which each line corresponds to a specific choice of two simple positive integers, n and m . If we pick any two small integers (1, 2, 3, ...) for n and m , we can calculate a frequency ν , from the equation:

$$\nu = R \times \left(\frac{1}{n^2} - \frac{1}{m^2} \right)$$

This is called the Rydberg equation, and the constant **R** is called the Rydberg constant, which has value $3.29 \times 10^{15} \text{ sec}^{-1}$. This is a truly remarkable equation, both because it is so simple and because it is complete. Every choice of n and m will produce a value of ν which is observed experimentally. And every ν that is observed in the experiment corresponds to a choice of n and m . There are no exceptions, no simple choices of n and m which don't produce a frequency observed in the spectrum, and no frequency in the spectrum for which we can't find simple choices of n and m .

A very interesting question, then, is what n and m mean. They must have some physical significance to the hydrogen atom, since they predict a physical property of the hydrogen atom. The spectrum alone does not provide any further insights, so we'll need additional observations.

What about the spectrum of atoms of other elements? Experimentally, we find that the atomic spectrum of every element consists of a limited set of frequencies which are observed. Each element has a unique atomic spectrum, which is a set of frequencies which uniquely identify that element. However, the Rydberg equation only predicts the frequencies for the hydrogen atom spectrum. There does not exist a similarly simple formula for any other atom.

Observation 2: The Photoelectric Effect

To understand the spectrum of hydrogen and other elements, we need to have a better understanding of the energy associated with electromagnetic radiation. To begin, we should be clear that electromagnetic radiation is a form of energy. There are some simple ways to see this in everyday life, including the fact that water left in sunlight will become hotter just as if it had been heated over a flame. It is also possible to generate electrical power from light, and it is even possible to “push” an object using energy absorbed from light. The question we now ask is, “How much energy is contained in light?” Even more specifically, “How is the energy contained in the light related to the frequency and intensity of the light source?”

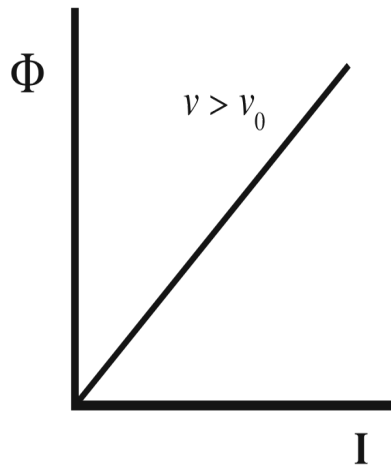
We need a way to measure the energy. One way is via the “photoelectric effect.” When light is directed at a metal surface under the correct conditions, experimental observations show that electrons are ejected from the metal. These electrons can be collected to produce a usable electric current. There are a number of simple applications of the photoelectric effect, including in remote control devices or “electric eye” door openers.

We already know that removing an electron from an atom requires energy, so it must be true that removing an electron from a metal requires energy, as well. In the photoelectric effect, the energy required is provided by the light source. We can vary the frequency of the light source and the intensity of the light source to determine under what conditions enough energy is provided to eject an electron from the metal. This could be detected by measuring the electric current produced. The more electrons ejected, the greater the current. We can also measure the energy of the ejected electrons. This is hard to do, but it is possible to measure the kinetic energy of these electrons as they are collected.

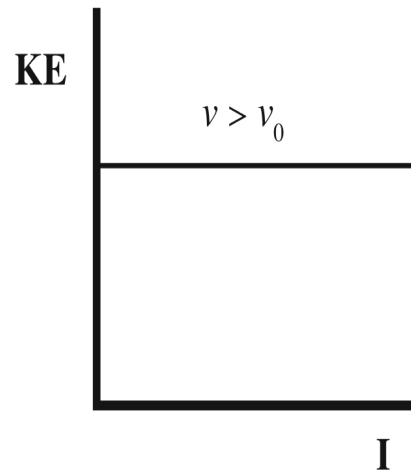
Before looking at the experimental data, we can stop to make a prediction about the results. We know that more intense light must contain greater energy, since light from the sun can certainly warm something up faster than a flashlight. So we would expect that more intense light would produce more and faster electrons. What would be harder to predict is the effect of changing the frequency of the light. So first, let’s use a light source with a single frequency. This can be done by passing the light source first through a prism or diffraction grating. Then we can vary the intensity of the light.

The first surprising result is that, if we choose a frequency too low for our source, there are no electrons produced by the photoelectric effect. There is no current at all. We have to use a light source with at least a minimum frequency, ν_0 , called the “threshold frequency,” in order to observe electrons ejected. This is puzzling. Even when we apply a very intense light source, which presumably provides a lot of energy, no electrons are ejected unless we are using light of at least the minimum frequency. And conversely, even if the intensity is very low so that not much energy is provided, we do get electrons ejected if the light source has frequency above the threshold. This is not what we would expect.

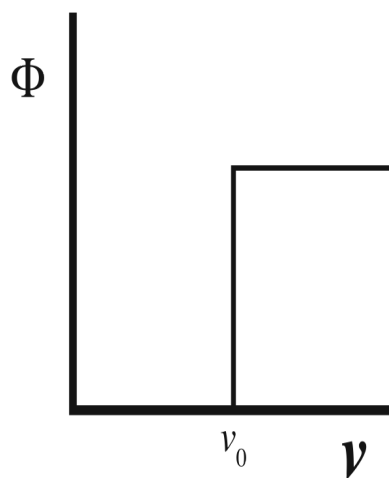
The value of the threshold frequency depends on which type of metal we shine the light source on. Let's stick with a single type of metal, and let's use a light source with frequency greater than the threshold, so $\nu > \nu_0$. With this light source in place, we'll vary the intensity of the light and measure the current and the kinetic energy of the ejected electrons. The results are shown in [\[link\]](#).



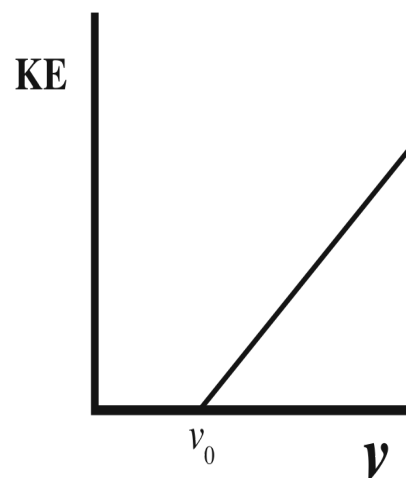
(a)



(b)



(c)



(d)

The results from shining light on metal and measuring the photoelectrons ejected. Φ is the photoelectric current, ν is the frequency of light, I is the intensity of incident light, and KE is the photoelectron kinetic energy. (a) If the frequency of light is high enough, the number of photoelectrons emitted increases directly with the light intensity. (b) However, the energy of the photoelectrons does

not depend on the light intensity. (c) For photoelectrons to be emitted, the light frequency must be greater than a threshold value. (d) If the light frequency is high enough, the energy of the electrons increases directly with the frequency.

In part (a), we see that, just as expected, a more intense light above the threshold frequency produces more electrons and a greater current. But in part (b), we see that the more intense light above the threshold frequency does not produce electrons with greater kinetic energy. This is not expected, since more energy would have been expected to produce more energetic electrons.

To dig further into these surprising results, let's fix the intensity of the light and vary the frequency of the source while observing the electric current produced and the kinetic energy of the electrons ejected. The results are also shown in [\[link\]](#). First, in part (c), we see the threshold frequency clearly. If the frequency is below the threshold frequency, ν_0 , then no electrons are ejected and there is no current. This suggests that the frequency of the light is related to the energy of the light so that we need a high enough frequency to provide a high enough energy. But part (c) also shows that if the light source is above the threshold, then we get a fixed current, no matter how high the frequency. This also seems strange if the higher frequency light is higher in energy. What happened to the added energy at high frequency? The answer is in part (d), which shows that the kinetic energy of the ejected electrons increases when we increase the frequency of the light source. In fact, it is a very simple relationship. Assuming the frequency is above the threshold, increasing the frequency of the light increases the kinetic energy of the electrons in direct proportion.

To summarize the results in [\[link\]](#), light which is high intensity but low frequency will not eject electrons. Light which has sufficiently high frequency will eject electrons whether the intensity is low or high. Increasing the intensity gives us more electrons but not more energetic electrons. Increasing the frequency gives us more energetic electrons but not more of them.

This is a very challenging puzzle, and an analogy helps to reveal the subtle answer. Imagine trying to knock pieces out of a wall by throwing objects at it. We discover that, no matter how many ping pong balls we throw, we cannot knock out a piece of the wall. On the other hand, only a single bowling ball is required to accomplish the task. This is because, in either case, the energy from either the ping pong balls or the bowling ball is provided to the wall in individual collisions. Each ball hits the wall individually, whether there are many of them or only one. The key to understanding our imaginary experiment is in discovering that, although there are many more ping-pong balls than bowling balls, it is only the impact of each individual particle with the wall which determines what happens and whether a piece of the wall is knocked loose.

The results of this “experiment” are similar to the observations of the photoelectric effect: very little high frequency light can accomplish what an enormous amount of low frequency light cannot. If we use this analogy, we can reasonably conclude that the energy of the light is supplied in “bundles” or “packets” of constant energy, similar to the energy of the balls being provided in packets. In light, we will call the packets of constant energy “photons.” In the photoelectric effect, each photon or packet of light energy hits the metal surface individually and acts individually.

How much energy does a photon contain? This is revealed by looking at [\[link\]](#)(d), which shows that the kinetic energy of the ejected electrons increases in direct proportion to the frequency provided that the frequency is above the threshold. We can conclude that the light supplies energy to the electron, which is proportional to the light frequency, so the energy of each photon is proportional to the frequency of the light. This now accounts for the observation that the frequency of the light source must be above the threshold frequency. For a photon to dislodge a photoelectron, it must have sufficient energy, by itself, to supply to the electron to overcome its attraction to the metal. It does not get any help from other photons, just like a single ping-pong ball acts alone against the wall. Since each photon must have sufficient energy and since the energy is proportional to the frequency, then each photon must be of a sufficient minimum frequency.

Increasing the intensity of the light certainly must increase the total energy of the light, since we observe this in everyday life. This means that the intensity of the light is proportional to the number of photons in the light but not the energy of each individual photon. Therefore, if the frequency of the light is too low, the photon energy is too low to eject an electron. Think again of the analogy: we can say that a single bowling bowl can accomplish what many ping-pong balls cannot, and a single high frequency photon can accomplish what many low frequency photons cannot.

The important conclusion for our purposes is that light energy is “quantized” into packets of energy. The amount of energy in each photon is proportional to the frequency of the light. Einstein first provided these conclusions, along with the equation which gives the energy of a photon of frequency ν

$$E = h\nu$$

where h is a constant called Planck’s constant.

Observation 3: Quantum Energy Levels in Hydrogen Atoms

Observation 1 showed us that only certain frequencies of light are emitted by hydrogen atoms. Observation 2 showed us that the energy of light is quantized into photons, or packets of energy, whose energy is proportional to the frequency of the light ν . We can now think about combining these two observations into a single observation about the hydrogen atom. When a hydrogen atom emits light, it must be emitting a photon of energy and is therefore losing energy. A hydrogen atom consists only of a nucleus and a single electron moving about that nucleus. The simplest (and perhaps only) way for the hydrogen atom to lose energy is for the electron to lose some of its energy. Therefore, when a hydrogen atom emits radiation of a certain frequency, it is emitting a photon of a specific energy, and therefore, the electron loses that same very specific energy.

In the spectrum of hydrogen, only certain frequencies are emitted. That means that only certain amounts of energy loss are possible for the electron in a hydrogen atom. How can this be? Why can’t an electron in a hydrogen

atom lose any amount of energy? The answer becomes clearer by thinking of an analogy, in this case of walking down a staircase or walking down a ramp. When you walk down a ramp, you can change your elevation by any amount you choose. When you walk down a staircase, you can only change your elevation by fixed amounts determined by the fixed heights of the steps and the difference in heights of those steps. The energy of an electron is like the height of each step on a staircase, not like the height on a ramp, since the energy can only be changed by certain specific amounts. This means that the energy of an electron in a hydrogen atom can only be certain specific values, called “energy levels.” In other words, the energy of a hydrogen atom is “quantized.”

The Rydberg equation tells us what these energy levels are. Recall that every frequency emitted by a hydrogen atom is predicted by the simple equation:

$$\nu = R \times \left(\frac{1}{n^2} - \frac{1}{m^2} \right)$$

Each emitted frequency must correspond to a certain energy $h\nu$, and this energy must be the energy lost by the electron. This energy must therefore be the difference between two electron energy levels in the hydrogen atom. Let's label the energy the electron starts with as E_m , where m is just an index that tells us where the electron starts. Similarly, let's label the energy the electron finishes with as E_n , where n is just a different index. The electron loses energy equal to $E_m - E_n$, and this must equal the photon energy emitted:

$$h\nu = E_m - E_n$$

We should be able to compare these two equations, since both contain a difference between two quantities that depend on two indices, m and n . Each energy of the electron might be given by an index n as

$$E_n = -h \times R \times \frac{1}{n^2}$$

If so, then the energy lost by an electron in the second equation above would be

$$E_m - E_n = -h \times R \times \left(\frac{1}{m^2} - \frac{1}{n^2} \right) = h\nu$$

This equation is the same as the Rydberg equation found experimentally. Therefore, we can conclude that, in a hydrogen atom, the energy of an electron can only be certain values given by an integer index n and equal to

$$E_n = -h \times R \times \frac{1}{n^2}$$

This means that the electron in a hydrogen atom can only exist in certain states with certain energies. These states must therefore determine the motion of the electron in the atom. Interestingly, this state of the electron is characterized by an integer, n , which we will now call a “quantum number” since it completely determines the quantized energy of the electron.

This discussion has only been about the hydrogen atom. These results also apply generally to all atoms, since all atoms display only specific frequencies which they emit or absorb. Since only certain frequencies can be emitted by each atom, only certain energy losses are possible, and only certain energy levels are possible in each atom. However, the equation above applies only to the energy of a hydrogen atom, since the Rydberg equation only describes the experimental spectrum of a hydrogen atom.

Review and Discussion Questions

1. The photoelectric effect demonstrates that radiation energy is quantized into “packets” or photons. Explain how and why this observation is of significance in understanding the structure of atoms.
2. Explain how we can know that higher frequency light contains higher energy photons.

By John S. Hutchinson, Rice University, 2011

Electron Orbitals and Electron Configurations in Atoms

Introduction

In looking at the structure of atoms to understand their properties, we have come up with two very powerful models. The first of these, the electron shell model developed in Concept Development Study 4, is based on observing the Periodic Law and the ionization energies of atoms. This led us to a model of the atom in which the electrons in an atom can be grouped together into “shells” with the electrons in a single shell seem to have similar energies. The second model is the quantum energy level description we observed in Concept Development Study 5. We observed that electrons in hydrogen atoms can only have certain specific energies, called energy levels. These two models seem quite similar. In both cases, it appears that the arrangement of the electrons in an atom can be understood by looking at the energies that the electrons can have.

But there are still many questions about how these two models are related. We developed the shell model by comparing the properties of different atoms, each with different numbers of electrons. We developed the quantum energy level model by looking mostly at hydrogen atoms, which each have only a single electron. We would like to know how the energy levels in a hydrogen atom are related to the electron shells in atoms with many electrons.

Perhaps the electrons in a single shell are in the same energy level, but we have not shown that. Even if we assume it is true, we still do not know what determines how many electrons can be in a single level. Without that, we do not know why each shell has a limit on how many electrons can fit. And if we don't know that, then we don't know why the properties of the elements are periodic.

To answer these important questions, we need to understand what it means for an electron to move about a nucleus. In the process of studying this, we will find that electrons move very differently than the ways in which we are used to particles moving. The results are surprising but they provide a firm foundation for understanding the Periodic Law of the elements.

Foundation

In this study, we will assume that we know the postulates of the Atomic Molecular Theory and our measurements of relative atomic masses. We will also assume that we know that structure of an atom, with a tiny, massive, positively charged nucleus surrounded by a much larger empty space in which electrons move. The positive charge on the nucleus is equal to the number of protons in the nucleus and, in a neutral atom, is also equal to the number of electrons moving about the nucleus. We will assume knowledge of the concept of electron shells as a means of understanding the Periodic Law, which describes the chemical and physical properties of the elements.

From the previous Concept Development Studies, we shall also assume an understanding of Coulomb's Law to describe the interactions of the protons and electrons in an atom. We will assume an understanding that light is an electromagnetic wave, meaning that, as it travels, the electric part of the light and the magnetic part of the light oscillate like a wave. And we shall also assume an understanding of the conclusions of our observations of the photoelectric effect. This means we understand that the energy of light is quantized into photons, or packets of energy, whose energy is proportional to the frequency of the light.

Observation 1: Electron waves and the uncertainty principle

Our first step in discovering how electrons move requires us to examine the results of an experiment seemingly far removed from the questions we are asking. These results concern something called "diffraction," which happens when two waves collide. When two particles collide, they may bounce off of each other, stick together, or cause each other to change paths. A wave collision is perhaps hard to think about, since waves don't exist in a single location. For this reason, we sometimes think instead of the overlap of two waves which come across each other. When two waves collide or overlap, their motions "interfere" with one another, meaning that the waves can add together or subtract from one another. This interference can be either constructive or destructive, depending upon how the waves add together. If the high points of both waves coincide in the same place, then the waves add together to give a bigger wave with a greater amplitude. If

the high point of one wave adds to the low point of the other wave, then the waves cancel each other out. We can have a wave with smaller amplitude, and in some locations the interference results in zero amplitude for the wave. This is called a “node.” It is easy to see these kinds of wave interference in water waves when the waves hit a barrier and bounce back. The wave coming to the barrier and the wave leaving the barrier interfere with each other, and a beautiful pattern of high points and low points emerges. [\[link\]](#) is an example of a “diffraction pattern.”

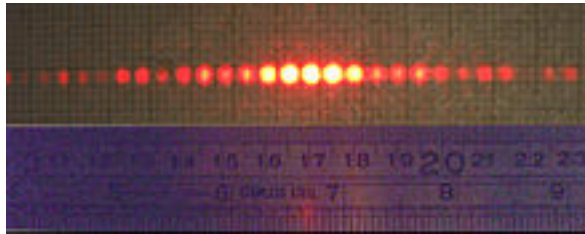


Photograph of wave interference coming towards the South Island
of New Zealand

(<http://www.flickr.com/x/t/0093009/photos/brewbooks/309494512/>)

A common way to observe interference with waves is to allow the wave to encounter an obstacle. For a light wave, this could be a small slit. Different pieces of the light wave encounter the slit at different points, deflecting in varying directions rather than going straight through the slit. When light is passed through a series or grid of small slits, the deflected light pieces can then interfere with one another either constructively or destructively,

depending upon the angle at which the light approaches the grid. Since we can get both increased and decreased amplitude, we can see a beautiful diffraction pattern, just like water waves and as seen in [\[link\]](#). Since the grid can produce a diffraction pattern, it is called a diffraction grating.

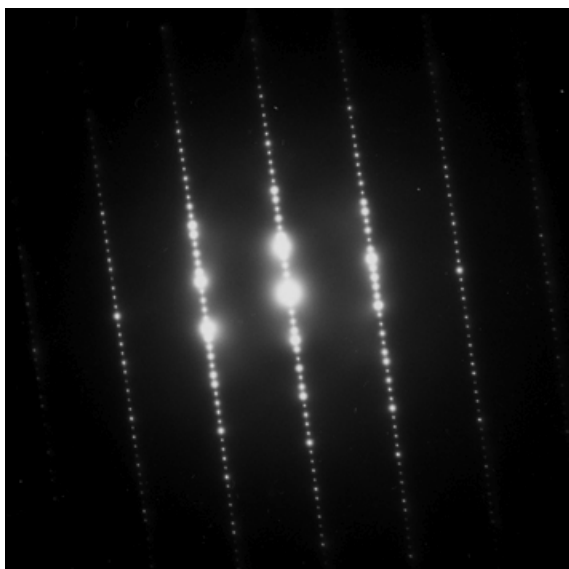


Diffraction of a red laser (633 nm) through a diffraction grating of 150 slits
(http://en.wikipedia.org/wiki/File:Diffraction_150_slits.jpg)

The comparison between the diffraction patterns of water waves and of light is very strong evidence to prove to us that light moves like a wave. Recall, however, that our earlier conclusion is that light behaves as a collection of energy packets, or photons. This means that light has some characteristics which are like particles and some which are like waves.

Up to this point, we have assumed that electrons are simply particles, behaving essentially as billiard balls or planets. To test this assumption, we try reflecting electrons off of a surface of a metal and looking at the pattern produced when the electrons return from their interaction with the surface. Since the metal consists of atoms, the metal surface looks to the incoming electron like a diffraction grating, with grooves spaced one atom apart. As we can see in [\[link\]](#), we observe in this experiment that the reflected electrons produce a pattern very similar to that observed by diffracted light. Certain angles of incidence and reflection produce no reflected electrons. These angles are alternated with angles with strong probability for

reflection of electrons. This is very strong evidence that electrons move as waves!

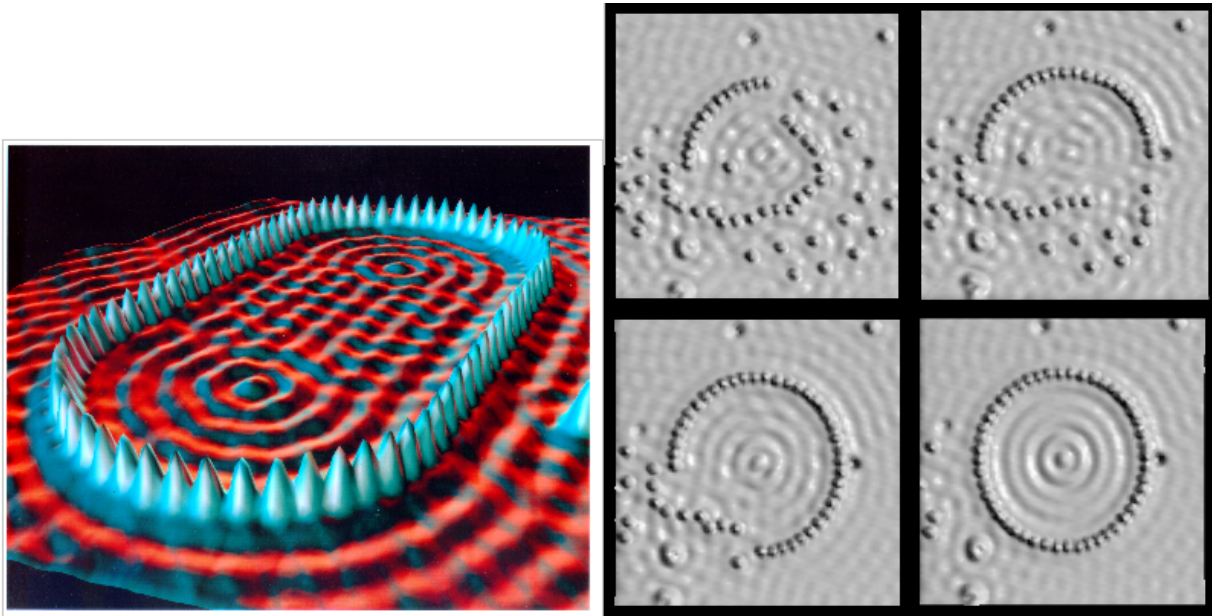


Electron diffraction pattern from parallel beams of electrons taken using a Transmission Electron Microscope

(<http://en.wikipedia.org/wiki/File:DifraccionElectronesMET.jpg>).

The concept of wave-like motion for electrons has been very difficult to imagine or visualize. What does it mean for a particle to move like a wave? This is very subtle, and we will discuss it later in this study. But we can visualize it. Very recently, scanning tunneling microscopy (STM) has been used to take images that clearly reveal this wave-like character. The STM mechanism can be used to literally pick up and place metal atoms in specific arrangements on metal surfaces. For example, iron atoms have been arranged to form a closed circle on a copper surface. An image of the resultant structure then taken using the STM shows not only the ring of iron atoms but also conspicuous waves inside the ring, which result from the

motion of electrons moving within the ring and reflecting off of the walls formed by the iron atoms. Two of the original images taken at IBM of these so-called “quantum corrals” are shown in [\[link\]](http://www.almaden.ibm.com/vis/stm/corral.html).



The color-enhanced STM image on the left shows iron atoms in a stadium corral shape on a copper surface. The series of four STM images on the right show the making of a circular corral of iron atoms on a copper surface. The images were originally created by IBM Corporation (<http://www.almaden.ibm.com/vis/stm/corral.html>)

Interpretation of the wave motion of electrons is a very complicated proposition, and we will only deal at present with a single important consequence, namely the uncertainty principle. A property of wave motion is that, unlike a particle, the wave does not have a definite position at a single point in space. By contrast, our everyday experience with particles is that the location of a particle is precise. We can look at something and determine where it is with a great deal of certainty. But our experiments tell us that the electron travels as a wave, and we cannot determine precisely the location of a wave. We must conclude that we cannot determine the precise

location of an electron in an atom. This is, for our purposes, the “uncertainty principle” arising from the branch of Physics called quantum mechanics. Even though we cannot determine the precise location of an electron within an atom, we can make measurements of the location of the electron. With these measurements, we find that each results in a different value for the location. Even though we can’t pin the electron down, we can determine a probability distribution for where the electron is observed.

This probability distribution is the most that we can know about the location and motion of an electron. It is extremely difficult to observe, but it can be determined by calculations from the field of quantum mechanics. The postulates (or rules) of quantum mechanics cannot be deduced from our experimental observations, and the calculations are far beyond what we need to worry about here. For what we need in this study, our observations, such as electron diffraction and the quantized energy levels for the electron in a hydrogen atom, are all consistent with the predictions of quantum mechanics. We will treat the predictions of quantum mechanics as the equivalent of experimental observations, conclusions that we can work with and build on.

Observation 2: Electron orbitals in hydrogen atoms

Quantum mechanics tells us that the motion of the electron in a hydrogen atom is described by a function, often called the “wave function” or the “electron orbital” and typically designated by the symbol Ψ . The electron orbital is the best information we can get about the motion of the electron about the nucleus. For a particular position (x,y,z) in the space about the nucleus, quantum mechanics tells us that $|\Psi|^2$ is the probability of observing the electron at the location (x,y,z) . The uncertainty principle we worked out above tells us that the probability distribution is the most we can know about the electron’s motion. In a hydrogen atom, it is most common to describe the position of the electron not with (x,y,z) but rather with coordinates that tell us how far the electron is from the nucleus, r , and what the two angles which locate the electron, θ and ϕ . We won’t worry much about these angles, but it will be valuable to look at the probability for the distance of the electron from the nucleus, r .

There isn't just one electron orbital for the electron in a hydrogen atom. Instead, quantum mechanics tells us that there are a number of different ways for the electron to move, each one described by its own electron orbital, Ψ . Each electron orbital has an associated constant value of the energy of the electron, E_n . This agrees perfectly with our earlier conclusions in the previous Concept Development Study. In fact, quantum mechanics exactly predicts the energy levels and the hydrogen atom spectrum we observe.

The energy of an electron in an orbital is determined primarily by two characteristics of the orbital. The first characteristic determines the average strength of the attraction of the electron to the nucleus, which is given by the potential energy in Coulomb's law. An orbital which has a high probability for the electron to have a low potential energy will have a low total energy. This makes sense. For example, as we shall see shortly, the lowest energy orbital for the electron in a hydrogen atom has most of its probability near the nucleus. By Coulomb's law, the potential energy for the attraction of the electron to the nucleus is lower when the electron is nearer the nucleus. In atoms with more than one electron, these electrons will also repel each other according to Coulomb's law. This electron-electron repulsion also adds to the potential energy, since Coulomb's law tells us that the potential energy is higher when like charges repel each other.

The second orbital characteristic determines the contribution of kinetic energy to the total energy. This contribution is more subtle than the potential energy and Coulomb's law. As a consequence of the uncertainty principle, quantum mechanics predicts that, the more confined an electron is to a smaller region of space, the higher its average kinetic energy must be. Remember that we cannot measure the position of electron precisely, and we define the uncertainty in the measurement as Δx . This means that the position of the electron within a range of positions, and the width of that range is Δx . Quantum mechanics also tells us that we cannot measure the momentum of an electron precisely either, so there is an uncertainty Δp in the momentum. In mathematical detail, the uncertainty principle states that these uncertainties are related by an inequality:

$$(\Delta x)(\Delta p) \geq \frac{h}{4\pi}$$

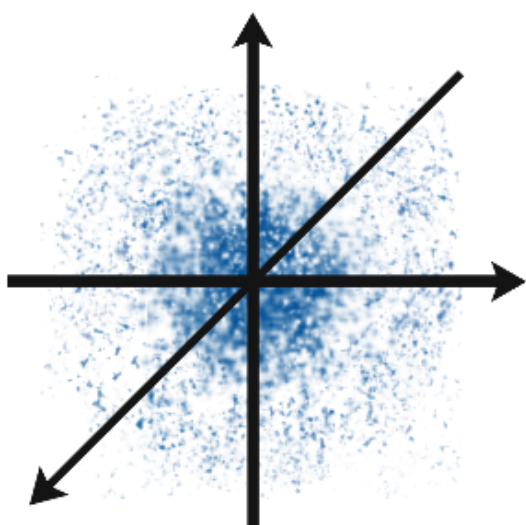
This inequality reveals that, when an electron moves in a small area with a correspondingly small uncertainty Δx , the uncertainty in the momentum Δp must be large. For Δp to be large, the momentum must also be large, the electron must be moving with high speed, and so the kinetic energy must be high. (We won't need to use this inequality for calculations, but it is good to know that h is Planck's constant, 6.62×10^{-34} J·sec. We have previously seen Planck's constant in Einstein's equation for the energy of a photon.)

From the uncertainty principle we learn that the more compact an orbital is, the higher the kinetic energy will be for an electron in that orbital. If the electron's movement is confined to a small region in space, its kinetic energy must be high. This extra kinetic energy is sometimes called the "confinement energy," and it is comparable in size to the average potential energy of electron-nuclear attraction. Therefore, in general, an electron orbital provides an energy compromise, somewhat localizing the electron in regions of low potential energy but somewhat delocalizing it to lower its confinement energy.

What do these orbitals look like? In other words, other than the energy, what can we know about the motion of an electron from these orbitals? Quantum mechanics tell us that each electron orbital is given an identification, essentially a name, that consists of three integers, n , l , and m , often called "quantum numbers." The first quantum number n tells us something about the size of the orbital. The larger the value of n , the more spread out the orbital is around the nucleus, and therefore the more space the electron has to move in. n must be a positive integer (1, 2, 3, ...), so the smallest possible n is 1. In a hydrogen atom, this quantum number n is the same one that tells us the energy of the electron in the orbital, E_n .

The second quantum number, l , tells us something about the shape of the orbital. There are only a handful of orbital shapes that we find in atoms, and we'll only need to know two of these for now. l is a positive integer or 0, and it must be smaller than the value of n for the orbital. For example, if n is 2, l must be less than 2, so l can be either 0 or 1. In general, l must be an integer from the set (0, 1, 2, ... $n-1$). Each value of l gives us a different orbital shape. If $l = 0$, the shape of the orbital is a sphere. Since the orbital tells us the probability for where the electron might be observed, a spherical

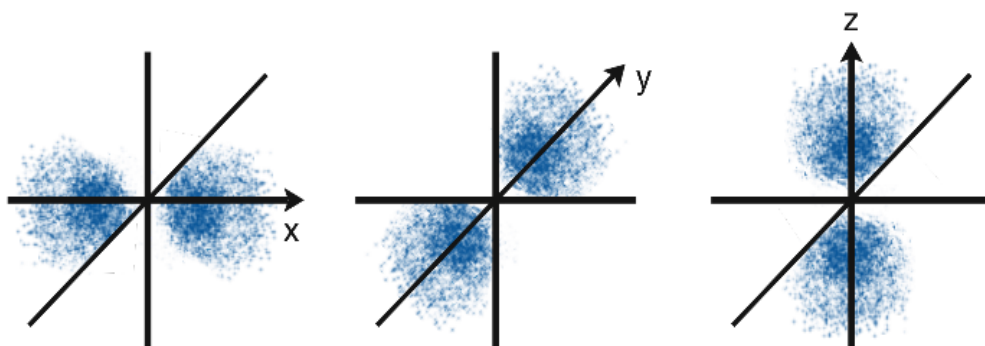
orbital means that the electron is equally likely to be observed at any angle about the nucleus. There isn't a preferred direction. Since there are only a few shapes of orbitals, each shape is given a one letter name to help us remember. In the case of the $l = 0$ orbital with a spherical shape, this one letter name is "s." (As an historical note, "s" doesn't actually stand for "sphere"; it stands for "strong." But that doesn't mean we can't use "s" as a way to remember that the s orbital is spherical.) [\[link\]](#) is an illustration of the spherical shape of the s orbital.



Approximate probability distribution of the 1s orbital shown with axes to emphasize the 3-dimensional spherical shape.

For now, the only other shape we will worry about corresponds to $l = 1$. In this case, the orbital is not spherical at all. Instead, it consists of two clouds or "lobes" on opposite sides of the nucleus, as in [\[link\]](#). This type of orbital is given the one letter name "p," which actually stands for "principal." Looking at the p orbitals in [\[link\]](#), it is reasonable to ask what direction the

two lobes are pointing in. If it seems that the lobes could point in any of three directions, that is correct. There are three “p” orbitals for each value of n , each one pointed along a different axis, x, y, or z. The third quantum number m gives each orbital a name allowing us to distinguish between the three orbitals pointing perpendicularly to each other. In general, the m quantum number must be an integer between $-l$ and $+l$. When $l = 1$, m can be -1, 0 or 1. This is why there are three p orbitals.



Approximate probability distributions of p orbitals shown along the x, y, and z axes.

Although we will not worry about the shape of the $l = 2$ orbitals for now, there are two things to know about them. First, these orbitals are given the single letter name d . Second there are five d orbitals for each n value, since $l = 2$ and therefore m can be -2, -1, 0, 1, or 2.

Chemists describe each unique orbital with a name which tells us the n and l quantum numbers. For example, if $n = 2$ and $l = 0$, we call this a 2s orbital. If $n = 2$ and $l = 1$, we call this a 2p orbital. Remember though that there are three 2p orbitals since there are three m values (-1, 0, 1) possible.

The motion of an electron in a hydrogen atom is then easily described by telling the quantum numbers or name associated with the orbital it is in. In our studies, an electron can only be in one orbital at a time, but there are many orbitals it might be in. If we refer to a 2p electron, we mean that the

electron is in an orbital described by the quantum numbers $n = 2$ and $l = 1$. The $n = 2$ value tells us how large the orbital is, and the $l = 1$ value tells us the shape of the orbital. Knowing the orbital the electron is in is for now everything that we can know about the motion of the electron around the nucleus.

Observation 3: Photoelectron spectra and electron configurations

So far, we have been concerned almost entirely with describing the motion of the electron in a hydrogen atom. Fortunately, this will be helpful in understanding the motion of electrons in all other atoms. The most important differences between the hydrogen atom and all other atoms are the charge on the nucleus, the number of electrons, and the effects of the repulsions of the electrons from each other. Electron-electron repulsion is not important in a hydrogen atom since it contains only a single electron, but it is very important in all other atoms.

To begin to understand the energies and orbitals for electrons in other atoms, we need more experimental information. We look at a new experiment called photoelectron spectroscopy. This form of spectroscopy is similar to the photoelectric effect we discussed in the previous concept study. We shine light on an atom and measure the minimum frequency of light which will ionize an electron from an atom. Remember that the frequency of light corresponds to a specific energy of the photons in that light. When the frequency of light is too low, the photons in that light do not have enough energy to ionize electrons from an atom. As we increase the frequency of the light, we find the minimum frequency, or threshold, at which electrons begin to ionize. As we continue to increase the frequency, we find that additional electrons are ionized at higher thresholds. These electrons are more tightly bound to the atom, requiring more energy and thus a greater frequency of light to ionize. By finding these higher thresholds for ionization, we can measure the ionization energy of not only the outermost electron but also of each electron in each orbital. With a higher frequency of light, there is sufficient energy to ionize a number of different electrons, each with its own energy. The different types of electrons are distinguishable from each other by their kinetic energies when

they are ionized. The more energy which is required to ionize the electron, the less energy is left over for the kinetic energy of the ionized electron. This means that we can look at the energies of all of the electrons in an atom, not just the electrons with the highest energy.

The threshold ionization energies for the first twenty elements are given in [\[link\]](#).

Element	Ionization Energy Thresholds (MJ/mol)					
H	1.31					
He	2.37					
Li	6.26	0.52				
Be	11.5	0.90				
B	19.3	1.36	0.80			
C	28.6	1.72	1.09			
N	39.6	2.45	1.40			
O	52.6	3.12	1.31			
F	67.2	3.88	1.68			
Ne	84.0	4.68	2.08			
Na	104	6.84	3.67	0.50		

Element	Ionization Energy Thresholds (MJ/mol)					
Mg	126	9.07	5.31	0.74		
Al	151	12.1	7.79	1.09	0.58	
Si	178	15.1	10.3	1.46	0.79	
P	208	18.7	13.5	1.95	1.01	
S	239	22.7	16.5	2.05	1.00	
Cl	273	26.8	20.2	2.44	1.25	
Ar	309	31.5	24.1	2.82	1.52	
K	347	37.1	29.1	3.93	2.38	0.42
Ca	390	42.7	34.0	4.65	2.9	0.59

Threshold Ionization Energies

There is a lot of data in this table, so we should take it line by line and look for patterns. We note that there is a single threshold for hydrogen and helium. In hydrogen, this makes sense, because there is only a single electron. The lowest energy orbital is the 1s orbital, since $n = 1$ is the lowest value and only $l = 0$ is possible when $n = 1$. But helium has two electrons. Why is there only a single type of electron in helium? It must be the case that both electrons in helium are in the same orbital with the same energy. Also, the ionization energy for helium is about double the ionization energy of hydrogen. This makes sense when we remember that the charge on the nucleus is in Coulomb's law: doubling the charge should double the strength of the attraction of the electron to the nucleus. This very strongly indicates that the two electrons in helium are in the same orbital as the one electron in hydrogen. If we want to describe the helium atom, we could state that it has two 1s electrons. We adopt a shorthand notation for this, $1s^2$, meaning that there are two electrons in the 1s orbital. This is called the

electron configuration of helium. This is an extremely important conclusion because it tells us that we can use the electron orbitals for the hydrogen atom to describe the motions of electrons in other atoms.

We now look at lithium and beryllium and notice that there are two ionization energies for each, meaning that there are two types of electrons in each atom. In lithium, this definitely means that the electron configuration is not $1s^3$. Apparently, there cannot be three electrons in a $1s$ orbital, so the third electron must go into a higher energy orbital. The next orbital higher in energy would be either a $2s$ or a $2p$ orbital. So lithium must have two electrons in the $1s$ orbital and one electron in either the $2s$ or $2p$ orbital, and the electron configuration is either $1s^22s^1$ or $1s^22p^1$. Whichever it is, it appears that beryllium will have a similar electron configuration $1s^22s^2$ or $1s^22p^2$, since there are only two ionization energies for beryllium. And we already know that two electrons can be in the same orbital. But which is the correct electron configuration?

To find out, we look at boron and notice that suddenly there are three ionization energies. One of them is much larger than the other two, and the other two are fairly similar. Certainly the large ionization energy is due to two electrons in the $1s$ orbital. It seems probable that one of the other two ionization energies is for an electron in the same orbital as lithium or beryllium. The third one represents an electron in a new orbital. Apparently, we cannot put a third electron into whichever orbital beryllium has two electrons in. This is just what we saw before: there appears to be a fundamental principle that only two electrons can move in the same electron orbital. This principle is part of a more general principle called the “Pauli Exclusion Principle,” named after its discoverer.

We can use this principle and the ionization energies to determine the electron configurations of lithium, beryllium, and boron. If beryllium’s configuration was $1s^22p^2$, we could put a third electron in a $2p$ orbital, because there are three $2p$ orbitals, as we recall from above. This would mean that boron’s electron configuration would be $1s^22p^3$, and there would be only two ionization energies. But this is not right: the data show that there are three ionization energies for boron. If beryllium’s electron configuration were $1s^22s^2$, then the added electron in boron would have to

go into a new orbital, and boron's electron configuration would be $1s^2 2s^2 2p^1$. The data in [\[link\]](#) for boron match this configuration. Notice that it appears that the 2s electrons and the 2p electron have very similar ionization energies. This makes sense, since both have the same n value. We will later explore the reason why they don't have exactly the same energy.

Does this concept account for the ionization energies of the next several elements (carbon to neon)? In each of these elements, there are only three ionization energies, and just as in boron, one is very large and the other two are smaller and comparable in size. But there are six elements from boron to neon. How can it be that we can have six electrons in the 2p orbital? The answer is that there are three 2p orbitals, so two electrons can move in each orbital for a total of six 2p electrons. For example, the electron configuration of neon would be $1s^2 2s^2 2p^6$.

The next obvious step in the data in [\[link\]](#) comes with sodium, where a fourth ionization energy is observed. This means that there are electrons in four different types of orbitals. If our reasoning above is correct, this makes sense. There is no room for a seventh electron to move in the 2p orbitals, so one electron in sodium must be in a higher energy orbital. The next higher energy orbital would be either 3s, 3p, or 3d, since $n = 3$ is the next lowest energy level. The ionization energies bear this out, since one of them is quite large (the 1s electrons) two of them are moderately sized (the 2s and 2p electrons), and one is much smaller (the $n = 3$ electron). Just by looking at the pattern of the ionization energies for the elements from sodium to argon, it should be clear that we have the same pattern as for lithium to neon. This means that the same argument must apply, and the 3s orbital must have an electron in sodium and must have two electrons in magnesium. Sodium's electron configuration must be $1s^2 2s^2 2p^6 3s^1$ and magnesium's must be $1s^2 2s^2 2p^6 3s^2$.

Our ionization energy data have provided us with three conclusions. First we conclude that two, and only two, electrons can move in the same orbital. Second, the electron configuration for each atom can be found by assigning electrons two at a time to each orbital in increasing order of energy, with the s orbital lower in the energy than the p orbital for each n value. This is

sometimes called the *aufbau* principle, after the German word meaning, roughly, “built up.”

Third is a very exciting conclusion based on the first two. Notice that when $n = 2$, there are four different orbitals to which we can assign a total of eight electrons. After those eight electrons have been assigned, no more electrons can be assigned to orbitals with $n = 2$. But we’ve seen this before! The number eight corresponds to our shell model of the atom in which only eight electrons could be in the second or third shell of each atom. Now we have an explanation of why the electron shells “fill up.” Each shell corresponds to a particular n value, and there are a limited number of electrons which can fit into the orbitals in each shell. Once those orbitals have all been assigned two electrons, the shell is “full,” and any additional electrons must be assigned to a new shell at a higher energy.

Looking at the pattern of the data in [\[link\]](#) reveals to us the ordering of the orbitals in terms of increasing energy, at least for this set of atoms. The data show that the orbitals, in order of increasing energy, are:

$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s$ etc.

Observation 4: The importance of electron-electron repulsion

There is a single detail missing from our description, which is of some importance to our discussion. Why is the 2s orbital lower in energy than the 2p orbital? This is something of a surprise. If we go back to look at the energy levels for an electron in a hydrogen atom, we will recall that the energy depends only on the n quantum number. This is the same for an electron in the 2s and 2p orbitals in a hydrogen atom. But in all of the atoms from lithium to neon, it is clear that the 2s orbital is lower in energy than the 2p orbital. Hydrogen is unique because it has only a single electron. As a result, there is no electron-electron repulsion to affect the energy.

Apparently, when there is electron-electron repulsion, an electron in the 2s orbital has a lower energy than an electron in the 2p orbital. Therefore, the movement of the electron in the 2s orbital must produce a smaller amount of electron-electron repulsion than that produced by the movement of the electron in the 2p orbital. Electrons do repel each other. If they move in

such a way as to maintain distance from one another, the amount of this repulsion is smaller. The 2s orbital must do a better job of this than the 2p orbital.

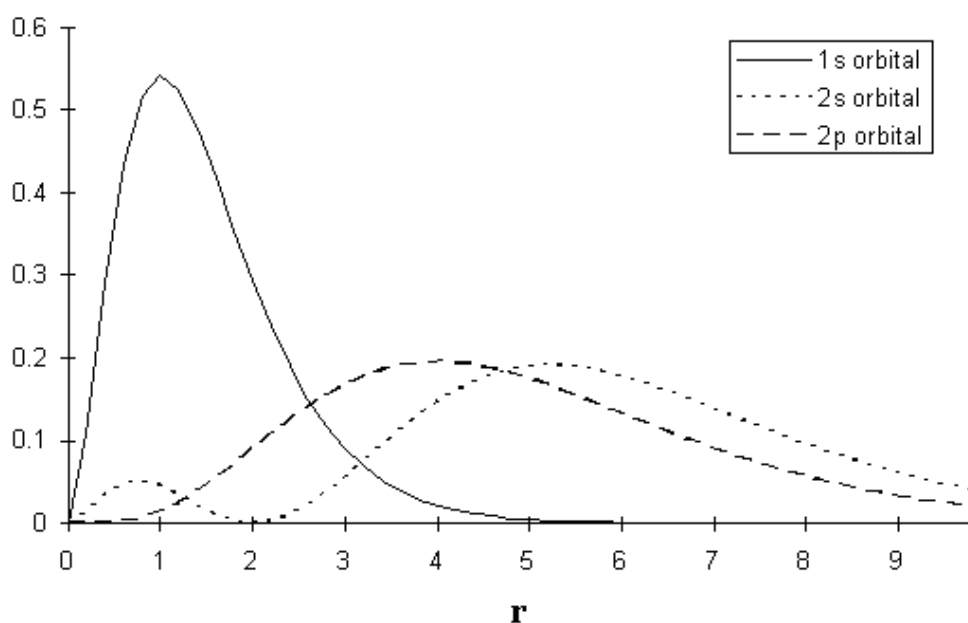
It is very difficult to calculate the energy from electron-electron repulsion because we do not know, on average, how far apart the electrons typically are so we can't use Coulomb's law in any simple way. We need a simple model instead. One way to do this is to think of the shell structure of the atom. An $n = 2$ electron is farther from the nucleus than an $n = 1$ electron. In lithium, for example, the lone 2s electron is on the outside of both the nucleus and the two 1s electrons. These two 1s electrons form a negatively charged "core" which surrounds the nucleus. In lithium, the nuclear charge is +3 and the charge on the core electrons is -2, so the 2s electron feels an attraction to a +3 charge and a repulsion from a -2 charge. A simple way to look at this is as though the 2s electron "feels" a net charge from the core of +1. This is sometimes called the "effective nuclear charge" because it takes into account both the attraction to the charge on the nucleus and the repulsion from the negative charge from the core electrons. In one way of viewing this, the nuclear charge is partially "shielded" by the negative charge of the core electrons, reducing the attraction of the 2s electron to the nucleus.

This argument would seem to apply perfectly well to an electron in either the 2s or 2p orbital, since both are in the $n = 2$ shell. So this does not account for the difference in the energies of these orbitals. It does account for the similarity of the energies of these orbitals, as clearly seen in the data in [\[link\]](#). But we still need to know why there is a difference.

The answer lies in remembering that in each orbital we only know the probabilities for where the electrons might be observed. Therefore, we cannot definitely state that the $n = 2$ electrons are "outside" of the 1s core electrons; we can only say that they probably are. As a result, the shielding effect is not perfect. In fact, there is some probability that an $n = 2$ electron might be found closer to the nucleus than the 1s electrons. This is called "core penetration." When an $n = 2$ electron does penetrate the core, it is no longer shielded from the nucleus. In this case, the $n = 2$ electron is very strongly attracted to the nucleus and its energy is thus lowered. Therefore,

the effect of core penetration is to reduce the shielding effect and therefore increase the effective nuclear charge.

What is the extent of this penetration? The answer is in [\[link\]](#), which shows the probability of finding an electron a distance r away from the nucleus for each of the 1s, 2s, and 2p orbitals. If we compare the probabilities, we see that there is a slightly greater probability (though still quite small) for the 2s electron to penetrate the core than for the 2p electron to do so.



Probability for an electron at a distance r from a hydrogen nucleus.

As a result of the core penetration, an electron in a 2s orbital feels a greater “effective nuclear charge” than just the core charge, which was approximated by assuming perfect shielding. Thus, the effective nuclear charge for a 2s electron is greater than the effective nuclear charge for a 2p electron. Therefore, the energy of an electron in the 2s orbital in beryllium is lower than it would be in the 2p orbital.

Knowing how the electrons move about the nucleus explains the ionization energy data in [\[link\]](#) and also explains the shell model of the atom by explaining why each shell can hold a limited number of electrons. This means that we can understand the Periodic Law and the trends in the Periodic Table using this new model. It turns out that we can also use our understanding of the motions of the electrons in atoms to help understand how and why atoms bond together to form molecules. This is a very important question for chemists, because understanding bonding is the key to understanding how and why molecules react with each other. Our understanding of electron orbitals will be very useful in answering these questions.

Review and Discussion Questions

1. Electron affinity is the energy released when an electron is attached to an atom. If an atom has a positive electron affinity, the added electron is attracted to the nucleus to form a stable negative ion. Why doesn't a Beryllium atom have a positive electron affinity? Explain how this demonstrates that the energy of a 2s orbital is less than the energy of a 2p orbital.
2. Why does an inert gas atom have a high ionization energy but a low electron affinity? Why do these properties combine to make the atoms of inert gases unreactive?
3. Consider electrons from two different subshells in the same atom. In photoelectron spectroscopy, the lower energy electron has a higher ionization energy but is observed to have lower kinetic energy after ionization. Reconcile the lower energy with the higher ionization energy with the lower kinetic energy.
4. Chlorine atoms have 5 distinct ionization energies. Explain why. Predict the number of ionization energies for Bromine atoms, and explain your answer. (Hint: examine the structure of the periodic table.)
5. Why does a Bromine atom have a much smaller radius than a Potassium atom, even though a Br atom has 16 more electrons than does a K atom?
6. Explain why electrons confined to smaller orbitals are expected to have higher kinetic energies.

7. Define "shielding" in the context of electron-electron repulsion. What is the significance of shielding in determining the energy of an electron? How is the affected by core penetration?

By John S. Hutchinson, Rice University, 2011

Covalent Bonding and Electron Pair Sharing

Introduction

The previous concept studies have provided us a detailed model for the structure and energetics of each atom of each element. This model is extremely useful in helping us understand how the chemical and physical properties of the elements are related to the properties of the individual atoms.

Chemistry, though, is mostly about molecules and how they react with one another, so we now turn our attention to understanding molecules. We should begin by reviewing what we know so far. Recall that there are over 50 million known compounds in our world, each made up from less than roughly 90 commonly occurring elements. From the atomic molecular theory, we understand what it means to form a compound from its component elements. A compound consists of identical molecules, with each molecule made up of the atoms of the elements in a simple whole number ratio. We call this ratio of atoms the molecular formula, and from our work on mass ratios, we also know how to determine what the molecular formula is for any compound of interest. From our work on chemical algebra, we can quantify chemical reactions, determining how much product can be produced from a given amount of reactant.

However, there are a great many fundamental questions about molecules we have not addressed or answered. Perhaps most interestingly, although we know what the molecular formula is for any compound, we don't know what determines the numbers of atoms which combine to form a molecule. Some combinations are observed (e.g. H_2O , H_2O_2) and others are never observed (e.g. H_6O , HO_6). We need to understand the principles which govern what combinations will work to form stable molecules and what combinations will not.

In order to answer these questions, we will need to develop an understanding of the forces which hold molecules together. Since atoms are neutral, the forces cannot simply be attractions of oppositely charged atoms. We know that there are diatomic molecules like H_2 and O_2 . Why would

identical atoms attract each other? Our knowledge of the charges contained inside atoms will be very helpful in understanding forces which bond atoms together. These forces must also be essential in determining the reactivity of a molecule, since these forces will determine how readily the atoms can be separated and recombined with atoms from other molecules. Predicting the reactivity of a substance is one of the great powers of Chemistry. If we wish to predict chemical reactivity of a particular substance, we must understand the forces which bond atoms together in a molecule.

Foundation

In this study, we will assume that we know the postulates of the Atomic Molecular Theory and our measurements of relative atomic masses. We know that an element is composed of individual atoms with identical masses, and we know that the atoms of different elements have different masses, which have been measured. From these masses, we can determine the molecular formula of any substance or compound of interest. As such, we'll assume that these are known.

We further assume the structure of the atom as a massive, positively charged nucleus, whose size is much smaller than that of the atom as a whole, surrounded by a vast open space in which negatively charged electrons move. These electrons can be effectively partitioned into a core and a valence shell, and it is only the electrons in the valence shell which are significant to the chemical properties of the atom. The number of valence electrons in each atom is equal to the group number of that element in the Periodic Table.

We will base much of our work on understanding the Periodic Law, which states that the chemical and physical properties of the elements are periodic functions of the atomic number. Finally, we will assume an understanding of Coulomb's Law, which describes the attractions and repulsions amongst charged particles.

Observation 1: Valence and the Octet Rule

To begin to understand chemical bonding, we will examine the valence of an atom, which is defined as the atom's most common tendency to form bonds to other atoms. We can figure these out by looking at some common molecular formulae for molecules formed by each atom. We'll start with the easiest case, the atoms of the noble gases. Since these atoms do not tend to combine with any other atoms, we will assign their valence as 0, meaning that these atoms tend to form 0 bonds. This doesn't really get us very far.

To find the valence of an atom which does form bonds, let's pick molecules which contain only a single atom of the type we're interested in and see how many other atoms it can combine with. Oxygen is a good place to start. For example, a single O atom will combine with two H atoms to form the most common molecule H_2O . Only under rare circumstances would we find any other combination of H and O in a neutral molecule. As such, it appears that the valence of an O atom is 2. Next we consider hydrogen, which combines with virtually any other element except the noble gases. Compounds containing hydrogen can contain a huge variety of the number of H atoms. However, molecules with a single H atom most typically contain only a single other atom, for example HF. A single C atom can combine with four H atoms, but a single H atom typically does not combine with more than one other atom. We do not typically see molecules like C_4H . A conspicuous feature of molecules containing hydrogen is that there are typically many more hydrogen atoms than other atoms. For example, hydrogen in combination with carbon alone can form CH_4 , C_2H_6 , C_8H_{18} , and many others. These observations lead us to conclude that an H atom has a valence of 1, meaning that a single H atom will typically only form 1 bond to another atom. This seems reasonable, since each H atom contains only a single proton and a single electron. This conclusion also is consistent with our conclusion that O atoms have a valence of 2, since the most common hydrogen-oxygen molecule is H_2O .

We can use hydrogen's valence of 1 to find the valence of other atoms. For example, the valence of C must be 4, since one C atom can combine with 4 H atoms, but not 5, and typically not 3. Nitrogen atoms have a valence of 3, to form NH_3 . Fluorine atoms have a valence of 1, to form HF molecules.

This concept also applies to elements just below carbon, nitrogen, oxygen, and fluorine. Silicon will form SiH_4 , so an Si atom has a valence of 4. Phosphorous forms PH_3 , so P has a valence of 3, and Sulfur forms H_2S , so S has a valence of 2. Each halogen atom (Cl, Br, I) prefers to form molecules by combining with a single hydrogen atom (e.g. HCl , HBr , HI), so each halogen has a valence of 1.

We can make further progress using the valence of the halogens. Lithium, sodium, potassium, and rubidium each bind with a single Cl atom to form LiCl , NaCl , KCl , and RbCl . Therefore, they also have a valence of 1. Because we also find that, for example, the combination of two potassium atoms with a single oxygen atom forms a stable molecule, our assignments are all still consistent, since oxygen's valence of 2 can be satisfied by the two K atoms, each with a valence of 1. We can proceed in this manner to assign a valence to each element by simply determining the number of atoms to which this element's atoms prefer to bind.

If we arrange the valences according to Periodic Table as in [\[link\]](#), we discover that there is a pattern. Just as we would expect from the Periodic Law, elements in the same group all share a common valence.

Li	Be	B	C	N	O	F	Ne
1	2	3	4	3	2	1	0
Na	Mg	Al	Si	P	S	Cl	Ar
1	2	3	4	3	2	1	0

Most Common Valence of Each Element in Periods 2 and 3

The inert gases with a valence of 0 sit to one side of the table. Each inert gas is immediately preceded in the table by one of the halogens: fluorine

precedes neon, chlorine precedes argon. And each halogen has a valence of one. This “one step away, valence of one” pattern can be extended. The elements just prior to the halogens (oxygen, sulfur, selenium, tellurium) are each two steps away from the inert gases in the table, and each of these elements has a valence of two (e.g. H_2O , H_2S). The elements just preceding these (nitrogen, phosphorus, antimony, arsenic) have valences of three (e.g. NH_3 , PH_3), and the elements before that (carbon and silicon most notably) have valences of four (CH_4 , SiH_4). The two groups of elements immediately after the inert gases, the alkali metals and the alkaline earths, have valences of one and two, respectively. Hence, for many elements in the periodic table, the valence of its atoms can be predicted from the number of steps the element is away from the nearest inert gas in the table. This systemization is quite remarkable and is very useful for remembering what molecules may be easily formed by a particular element.

Next we discover that there is an additional very interesting aspect to the pattern of the valences: for elements in Groups 4 through 8 (e.g. carbon through neon), the valence of each atom plus the number of electrons in the valence shell in that atom always equals eight. For instance, carbon has a valence of 4 and has 4 valence electrons; nitrogen has a valence of 3 and has 5 valence electrons; oxygen has a valence of 2 and has 6 valence electrons. We have made one of the most important observations in Chemistry, the “Octet Rule”:

Octet Rule: For elements in Groups 4 through 8 in Periods 2 and 3 of the Periodic Table, the valence of each atom plus the number of valence electrons in each atom is equal to 8.

Observation 2: Covalent Bonding

As a way to think about this pattern, remember that for each of the atoms in these two periods, the valence shell can accommodate eight electrons. It turns out that the valence of each atom in Groups 4 through 8 is equal to 8 minus the number of valence electrons the atom has. For example, the valence of an N atom is 3, which is equal to 8 minus the number of valence electrons in N, which is 5. This tells us that, for each of these atoms, the

number of bonds the atom typically forms is equal to the number of vacancies in its valence shell.

This suggests a model which would account for the Octet Rule. It appears that each atom in these Groups attempts to bond to other atoms so as to completely fill its valence shell with electrons. For elements in Groups 4 through 8, this means that each atom attempts to complete an “octet” of valence shell electrons. (Why atoms should behave this way is a question unanswered by this model.)

Consider, for example, the combination of two chlorine atoms to form Cl_2 . Each chlorine atom has seven valence electrons and seeks to add a single electron to complete an octet. Hence, chlorine has a valence of 1. Either chlorine atom could satisfy its valence by “taking” an electron from the other atom, but this would leave the other atom now needing two electrons to complete its valence shell. The only way for both atoms to complete their valence shells simultaneously is to share two electrons. Each atom donates a single electron to a shared electron pair. This sharing of electrons is what we call a chemical bond. More specifically, we call this a “covalent bond,” so named because the bond acts to satisfy the valence of both atoms. The two atoms are thus held together by the need to share the electron pair.

Let’s apply this to a molecule with an H atom, HCl . H atoms are not expected to have an octet. In fact, the valence shell in H can accommodate just two electrons. Because an H atom has 1 valence electron, it thus has a single vacancy, or a valence of 1. Our model for electron pair sharing works for H atoms as well. When H and Cl bond, they share a pair of electrons forming a covalent bond so that the H atom has a full valence shell (two electrons) and the Cl atom has a full valence shell (eight electrons).

We now have two important pieces of our model. First, atoms form a covalent bond by sharing a pair of electrons. Second, for atoms in Groups 4 through 8, they tend to share enough electrons to fill the valence shell with 8 electrons, and this determines the number of covalent bonds they form. An H atom shares one pair of electrons to form a single covalent bond.

Observation 3: Molecular Structures in Compounds of Carbon and Hydrogen

Many of the most important chemical fuels are compounds composed entirely of carbon and hydrogen, i.e. hydrocarbons. The smallest of these is methane CH_4 , a primary component of household natural gas. Other simple common fuels include ethane C_2H_6 , propane C_3H_8 , butane C_4H_{10} , pentane C_5H_{12} , hexane C_6H_{14} , heptane C_7H_{16} , and octane C_8H_{18} .

There is a very interesting consistency in these molecular formulae: in each case, the number of hydrogen atoms is two more than twice the number of carbon atoms, so that each compound has a molecular formula like $\text{C}_n\text{H}_{2n+2}$. (Try it out!) This suggests that there are strong similarities in the valences of the atoms involved which should be understandable in terms of our valence shell electron pair sharing model.

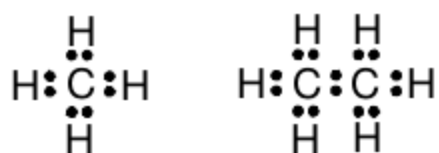
Since each H atom can only bond to a single other atom, the carbon atoms in each molecules must be directly bonded together. In the easiest example of ethane, the two carbon atoms are bonded together, and each carbon atom is in turn bonded to three hydrogen atoms. This would fit our model of valence, since each carbon atom is bonded to four other atoms (three hydrogens and the other carbon). By sharing an electron pair with each of those four atoms, each carbon atom fills its valence shell with eight electrons. This example was not difficult.

In most other cases, it is not so trivial to determine which atoms are bonded to which. This is because there may be multiple possibilities which satisfy all the atomic valences. As the number of atoms and electrons increases, it may also be difficult to determine whether each atom has an octet of electrons in its valence shell. We need a system of counting the valence electrons which makes it easy for us to see these features more clearly. To start, we create a notation for each atom which displays the number of valence electrons in the unbonded atom explicitly. In this notation, carbon and hydrogen look like



where the dots represent the single valence electron in hydrogen and the four valence electrons in carbon. Note that the C atom valence electrons are all unpaired. This is because we know that the valence of a C atom is four, so there are four valence electrons available to be shared with other atoms.

Using this notation, it is now fairly easy to represent the shared electron pairs and the carbon atom valence shell octets in methane and ethane. For each pair of bonded atoms, we share an electron pair from the valence shell electrons. This gives for methane and ethane:

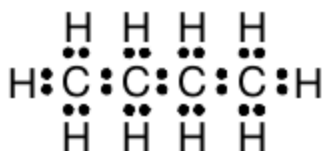


Recall that each shared pair of electrons represents a chemical bond. These drawing are examples of what are called “Lewis structures,” after G.N. Lewis who first invented this notation. These structures reveal, at a glance, which atoms are bonded to which, so we call this the “structural formula” of the molecule. There are two things to check about the electrons in the structural formula. First, we cannot have created or lost any valence electrons. For example, in ethane we started with four valence electrons from each carbon and one valence electron from each hydrogen, for a total of 14 electrons. The structural formula of ethane drawn above has 14 valence electrons, so that is correct. Second, if we have satisfied the valence of each atom, each carbon should have an octet of electrons and each hydrogen should have two electrons. We can also easily count the number of valence shell electrons around each atom in the bonded molecule and verify that this is also correct.

In a larger hydrocarbon, the structural formula of the molecule is generally not predictable from the number of carbon atoms and the number of hydrogen atoms, because there may be more than one possible arrangement.

In these cases, the molecular structure must be given to deduce the Lewis structure and thus the arrangement of the electrons in the molecule.

However, with this information, it is straightforward to create a Lewis structure for molecules with the general molecular formula C_nH_{2n+2} such as propane, butane, etc. For example, the Lewis structure for “normal” butane (with all carbons linked one after another) is found to be:



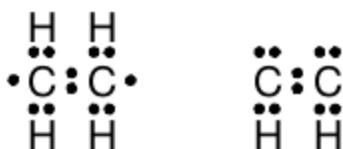
There are no hydrocarbons where the number of hydrogen atoms is greater than two more than twice the number of carbons. For example, CH_5 does not exist, nor does C_2H_8 . If we try to draw Lewis structures for CH_5 or C_2H_8 which are consistent with the octet rule, we will find that there is no way to do so. Similarly, CH_3 and C_2H_5 are observed to be so extremely reactive that it is impossible to prepare stable quantities of either compound. And again we will find that it is not possible to draw Lewis structures for these molecules which obey the octet rule.

We come to a very important and powerful conclusion: when it is possible to draw a Lewis structure in which each carbon has a complete octet of electrons in its valence shell, the corresponding molecule will be stable and the hydrocarbon compound will exist under ordinary conditions. After working a few examples, it is apparent that this always holds for compounds with molecular formula C_nH_{2n+2} .

Observation 4: Double and Triple Bonds in Compounds of Carbon and Hydrogen

Although our model so far does a good job of describing molecules with the formula C_nH_{2n+2} , there are many stable hydrocarbon compounds with molecular formulae in which the number of hydrogen atoms is less than $2n+2$. Simple examples are ethene C_2H_4 and acetylene C_2H_2 in which there

are not enough hydrogen atoms to permit each carbon atom to be bonded to four atoms each. In each molecule, the two carbon atoms must be bonded to one another. When we arrange the electrons so that the carbon atoms share a single pair of electrons and then attach hydrogen atoms to each carbon, we wind up with rather unsatisfying Lewis structures for ethene and acetylene:



Note that, in these structures, neither carbon atom has a complete octet of valence shell electrons, but these are both stable compounds. We need to extend our model to work for these types of molecules.

These structures indicate that the carbon-carbon bonds in ethane, ethene, and acetylene should be very similar, since in each case a single pair of electrons is shared by the two carbons. However, we can observe that the carbon-carbon bonds in these molecules are very different chemically and physically. First, we can compare the energy required to break each bond (the “bond energy” or “bond strength”). Second, it is possible to observe the distance between the two carbon atoms, which is referred to as the “bond length.” Bond lengths are typically measured in picometers (1 picometer (pm) = 10^{-12} m).

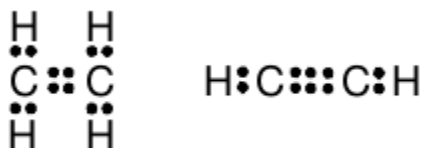
	Ethane	Ethene	Acetylene (Ethyne)
Bond strength (kJ/mol)	347	589	962

Bond length(pm)	154	134	120
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Properties of Carbon-Carbon bonds in Two Carbon Atom Molecules

Looking at the data, it is very clear that the bonding between the carbon atoms in these three molecules must be very different. The bond strength increases when there are fewer H atoms, and the bond length gets progressively shorter with fewer H atoms. These observations are reinforced by looking at carbon-carbon bond strengths and lengths in other C_nH_{2n+2} molecules, like propane and butane. In all of these molecules, the bond strengths and lengths are comparable to those in ethane.

The bond in ethene is about one and a half times stronger than the bond in ethane; this suggests that there might be a second bond between the two carbon atoms. This could be formed from the two unpaired and unshared electrons in the ethene structure above. Similarly, the bond in acetylene is about two and a half times stronger than the bond in ethane, so we can imagine that this results from the sharing of three pairs of electrons between the two carbon atoms. These assumptions produce the following Lewis structures:



These structures appear to make sense from two regards. First, these structures would explain the trend in carbon-carbon bond strengths as arising from the increasing number of shared pairs of electrons. Second, each carbon atom has a complete octet of electrons. Our model now reveals that there is a “double bond” in ethene and a “triple bond” in acetylene.

We thus extend our model of valence shell electron pair sharing to conclude that carbon atoms can bond by sharing one, two, or three pairs of electrons as needed to complete an octet of electrons, and that the strength of the bond is greater when more pairs of electrons are shared. Moreover, the data

above tell us that the carbon-carbon bond in acetylene is shorter than that in ethene, which is shorter than that in ethane. We conclude that triple bonds are shorter than double bonds, which are shorter than single bonds.

Observation 5: Hydrocarbon Compounds Containing Nitrogen, Oxygen, and the Halogens

Many compounds composed primarily of carbon and hydrogen also contain some oxygen or nitrogen, or one or more of the halogens. These include the majority of biomolecules, such as amino acids and proteins. This means that it would be very desirable to extend our understanding of bonding by developing Lewis structures for these types of molecules.

Recall that a nitrogen atom has a valence of 3 and has five valence electrons. In our notation, we could draw a structure in which each of the five electrons appears separately in a ring, similar to what we drew for C. However, our new understanding of covalent bonding tells us that unpaired electrons on atoms are shared with other atoms to form bonds. Having all five valence electrons in an N atom unpaired would imply that an N atom would generally form five bonds to pair its five valence electrons. Since the valence is actually 3, our notation should have three unpaired electrons. One possibility looks like:

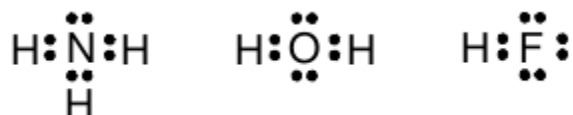


Note that this structure leaves three of the valence electrons “unpaired” and thus ready to join in a shared electron pair. The remaining two valence electrons are “paired,” and this notation implies that they therefore are not generally available for sharing in a covalent bond. This notation is consistent with the available data, i.e. five valence electrons and a valence of 3. Pairing the two non-bonding electrons seems reasonable in analogy to the fact that electrons are paired in forming covalent bonds.

We can draw similar structures for oxygen and fluorine. The other halogens will have structures like F, since they have the same valence and the same number of valence electrons.



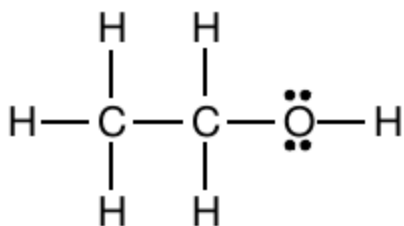
With this notation in hand, we can now analyze structures for molecules including nitrogen, oxygen, and the halogens. The hydrides are the easiest:



Note that the octet rule is clearly obeyed for oxygen, nitrogen, and the halogens.

At this point, it becomes very helpful to adopt one new convention: a pair of bonded electrons will now be more easily represented in our Lewis structures by a straight line, rather than two dots. Double bonds and triple bonds are respectively represented by double and triple straight lines between atoms. We will continue to show non-bonded electron pairs explicitly with two dots.

For example, ethanol has the molecular formula $\text{C}_2\text{H}_6\text{O}$. The two carbon atoms are bonded together and the oxygen atom is attached to one of the two carbons; the hydrogen atoms are arranged to complete the valences of the carbon atoms and the oxygen atom:



In this structure, each line connecting two atoms represents a shared pair of electrons, or a covalent bond. The non-bonding pairs on oxygen are often called “lone pairs.” It is important for us to include them in our structure for three reasons. First, including the lone pairs helps us check that we have drawn a structure with the correct number of valence electrons. Let’s check this for this drawing. Each carbon atom contributes four valence electrons, the oxygen atom contributes six, and each hydrogen atom contributes 1. There are thus a total of $2(4)+6+6(1)=20$ valence electrons. Counting electrons in the drawing, there are eight covalent bonds, each of which represents two valence electrons, and two lone pairs, for a total of 20 valence electrons.

Second, drawing the lone pairs helps us see that the octet rule is obeyed for the O atom. Third and perhaps most importantly, we will later learn that lone pairs of electrons are important in determining the physical and chemical properties of molecules.

Review and Discussion Questions

1. Compounds with formulae of the form C_nH_{2n+2} are often referred to as "saturated" hydrocarbons. Using Lewis structures, explain how and in what sense these molecules are “saturated.”
2. Molecules with formulae of the form C_nH_{2n+1} (e.g. CH_3 , C_2H_5) are called "radicals" and are extremely reactive. Using Lewis structures, explain the reactivity of these molecules.
3. State and explain the experimental evidence and reasoning which shows that multiple bonds are stronger and shorter than single bonds.
4. Compare N_2 to H_4N_2 . Predict which bond is stronger and explain why.

Molecular Structures

Introduction

We have developed a model by which we can understand molecular formulas. In the previous concept development study, we began by asking what determines which combinations of atoms will form stable molecules and compounds and why some combinations are never observed. We combined our knowledge of the electronic structures of atoms with our knowledge of molecular formulas and the common valences of atoms to develop the octet rule. The rule tells us that the most common valence of each main group atom is equal the number of spaces for electrons in the valence shell of the atom, which is eight minus the number of valence electrons. Thus, according to the octet rule, atoms tend to bond such that they have eight valence electrons in the bonded molecule. The Lewis structure model implements the octet rule and reveals which atoms are bonded to which other atoms in a molecule and whether these bonds are single, double, or triple bonds. Thus, Lewis structures provide additional information about molecules that we cannot learn just from molecular formulas.

This model of molecular structure, like most good scientific models, poses at least as many new questions as the questions it was designed to answer. What new information can be gleaned from our knowledge of the structure of a molecule? It seems reasonable for us to assume that the properties of a compound are related to the properties of the individual molecules of the compound. It also seems reasonable to assume that the properties of individual molecules are related to their structures. If we could identify the properties of molecular structures which are related to their chemical or physical properties, we could understand these properties and perhaps even design molecules which have interesting or valuable properties. This is one of the very most important questions in chemistry. Before we can pursue it, we need more detail and insight about molecular structures.

In this concept development study, we will examine various arrangements of atoms in a variety of molecules and look for common structures. We will find both variety and common features. We will also examine how the

electrons are arranged in these molecular structures. This will allow us to interpret molecular structures accurately.

Foundation

We will assume that we know the valences of the common main group elements, and from this, we know the octet rule. This assumes knowledge of the valence shell model of the electronic structure of atoms. We know that we can combine these atoms in the Lewis structure model to build molecular structures which satisfy the valences of the main group elements and fit the octet rule for valence electrons. We have found that molecules which have Lewis structures that fit the octet rule typically form stable compounds. And we found that, for combinations of atoms where we cannot construct Lewis structures that fit the octet rule, the compounds are either unstable or non-existent.

By comparing our molecular structures to experimental data, we observed that double bonds are stronger and shorter than single bonds, and triple bonds are stronger and shorter than double bonds.

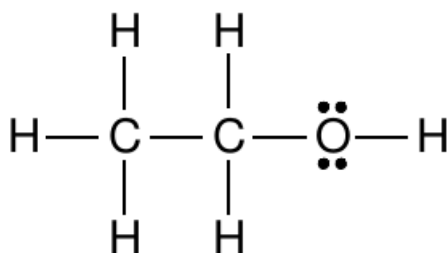
Observation 1: Compounds with Identical Molecular Formulas

In simple molecules, such as CH_4 , it is fairly clear that the molecule consists of a single carbon atom surrounded by and bonded to four hydrogen atoms. There really is only one way that the molecule could be structured. But even in molecules only slightly larger than this, we discover some interesting observations.

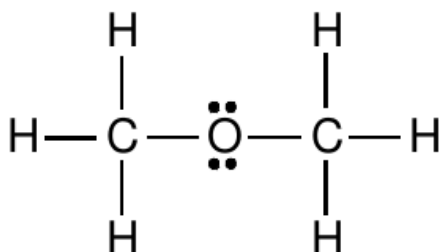
Let's consider the molecular formula $\text{C}_2\text{H}_6\text{O}$. Experimentally, we discover that there are two different compounds with the molecular formula $\text{C}_2\text{H}_6\text{O}$, and these two compounds have very different physical and chemical properties. One of the compounds is a liquid at room temperature with a boiling point of 78°C . The other is a gas with a boiling point of -25°C . This might seem surprising in a couple of ways. First, how could two compounds have the same molecular formula? We might have expected that a specific combination of the elements would produce a specific compound, but this is clearly not true. And second, even if we do imagine more than

one possible compound, we would most probably have guessed that they would be similar in their properties since they contain the same elements in the same proportions. How can two compounds with the same molecular formula have so very different properties?

To understand these observations, we can use our model for molecular structures. From our earlier work, it is clear that the two carbon atoms and the oxygen atom must be bonded together, surrounded by hydrogen atoms. But in what order are they bonded? One option would be C-C-O, and a second would be C-O-C. The first of these would give us the molecular structure:



The second would give us:

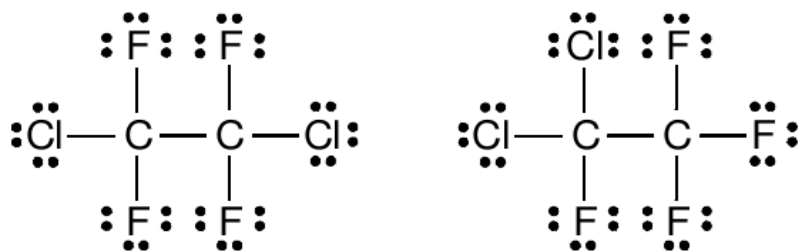


By all of our criteria for the Lewis model of molecular structures, both of these look right. Each carbon atom and the oxygen atom in each structure show the proper valence and a complete valence shell. There are no unpaired electrons in either structure. These two molecular structures must be consistent with our experimental observation that there are two

compounds with this molecular formula. Each of the compounds must correspond to one of the different molecular structures.

Which one is which? Determining which molecular structure corresponds to which compound is an interesting experimental problem. We'll explore this further in the next section. For now, we'll assume that it is experimentally possible to determine which is which. In this case, the first molecular structure above, containing the C-O-H arrangement, is the liquid at room temperature and is called ethanol or ethyl alcohol. The second molecular structure, containing the C-O-C arrangement, is a gas at room temperature and is called dimethyl ether.

Compounds with the same molecular formula are called "isomers" of one another. In the example above, dimethyl ether is an isomer of ethanol and vice versa. It is very common to observe isomers for any given molecular formula. Some of these are simple to see. Let's consider the molecular formula $C_2F_4Cl_2$. Each halogen atom generally has a valence of 1 with seven valence electrons. This suggests that the two carbon atoms should be bonded together, as in ethane, with the six halogen atoms arranged three per carbon. But there is more than one way to do this:

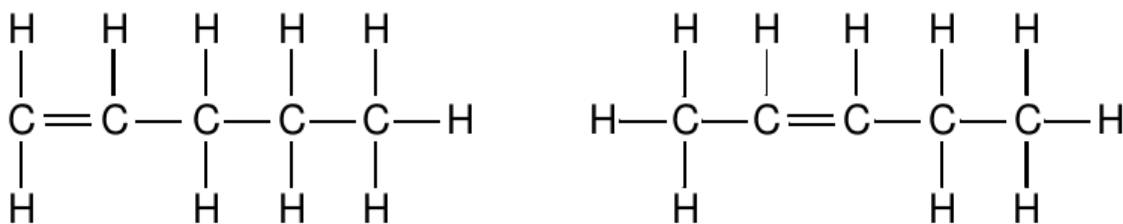


In one molecular structure, the two Cl atoms are on the same carbon atom. In the other, the two Cl atoms are separated on different carbon atoms. We might guess that this difference in arrangements does not matter, since in both cases, the F and Cl atoms are all bonded to the carbon atoms, and the carbon atoms are bonded together.

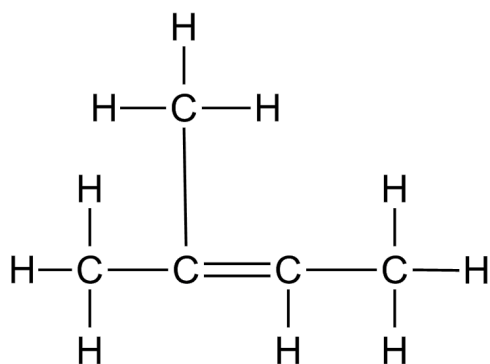
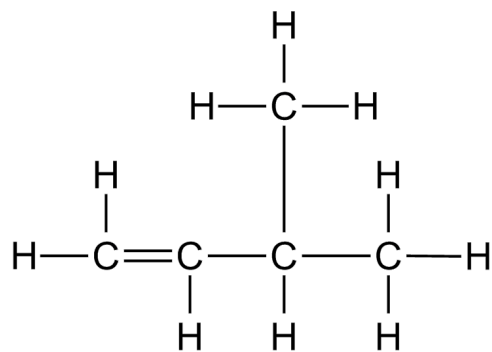
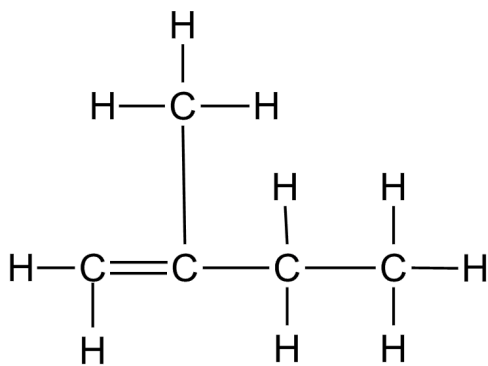
Our experimental observations prove this guess is wrong. There are two isomers of $C_2F_4Cl_2$, one with a boiling point of $3^\circ C$ and a melting point of

-57 °C and the other with a boiling point of 3.8 °C and a melting point of -94 °C. Differences in the arrangement of atoms in similar molecules clearly do matter, even if those differences don't seem all that great.

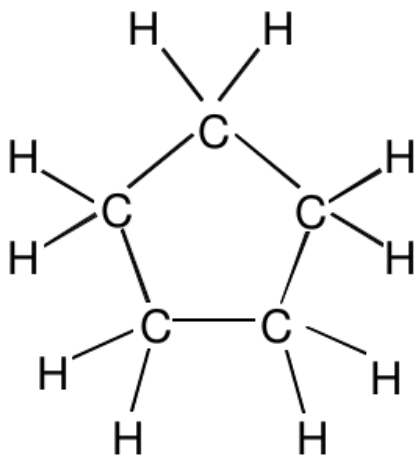
In some cases, isomers have very obviously different structures. Let's look at the various isomers with the molecular formula C_5H_{10} . Perhaps the simplest structure is one with a double bond between two of the carbon atoms. However, in a chain of five carbon atoms, there are two different places where the double bond might be. Each of these corresponds to a different compound:



The five carbon atoms don't have to be lined up in a single chain:



One isomer of C_5H_{10} which might not have been obvious is a structure in which the five carbon atoms form a ring:



All seven of these isomers are different compounds with distinct physical and chemical properties. From these and many similar observations we can

conclude as a general rule that isomers have different molecular structures, which give rise to the differing properties of the compounds.

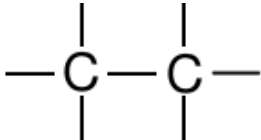
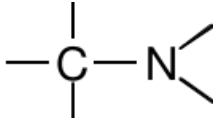
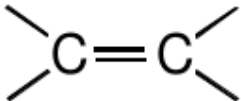
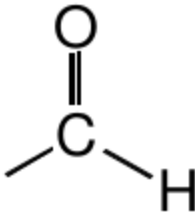

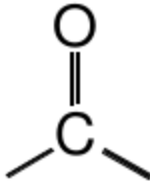
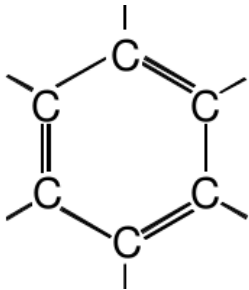
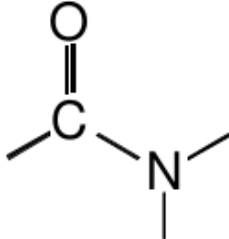
Observation 2: Molecular Properties and Functional Groups

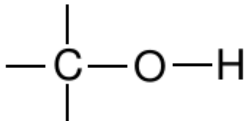
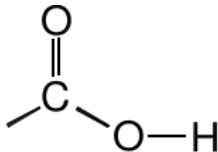
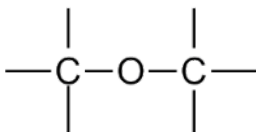
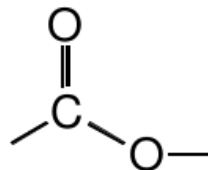
The previous conclusion leads us to a new question: what is it about the differences in molecular structure that produces the differences in properties? This is a huge question which, in many ways, is one of the fundamental questions of the field of Organic Chemistry. Although we cannot hope to provide all the answers to this question in this one study, we can study a few examples to develop the fundamental concept.

We begin by looking for common connections amongst molecular structures and molecular properties. From the observations we just discussed, it seems that every arrangement of the atoms in a molecule produces properties which are unlike the properties of any other molecular structure. Let's go back and examine the two isomers of C_2H_6O , ethanol and dimethyl ether. As noted above, ethanol is a liquid at room temperature, and is completely soluble in water. Dimethyl ether is a gas at room temperature and is less soluble in water than ethanol.

The most notable difference between the two molecular structures is that the oxygen atom is bonded to a hydrogen atom in ethanol. There are no O-H bonds in dimethyl ether. The structure C-O-H appears in a large number of molecules. And experimentally, we find that molecules with the C-O-H group have similar molecular properties to ethanol. All are liquids at room temperature and most are soluble in water. These compounds are, as a class, called alcohols. These observations lead us to conclude that common properties are due to the common C-O-H group. The C-O-H is called the "hydroxyl group". When we find a group of atoms which gives a specific set of properties, or "function," to molecules, we call that group of atoms a "functional group." Using this new term, we would say that the class of molecules called alcohols contain the hydroxyl functional group.

There are many functional groups found in chemistry, each of which gives specific properties to the class of molecules containing it.

Functional Group	Functional Group Structure	Functional Group	Functional Group Structure
Alkane		Amine	
Alkene		Aldehyde	
Alkyne		Ketone	
Arene		Amide	

Functional Group	Functional Group Structure	Functional Group	Functional Group Structure
Alcohol		Carboxylic Acid	
Ether		Ester	

As mentioned above, the field of Organic Chemistry is in large part about finding ways to synthesize new molecules containing specific functional groups which therefore form compounds with specific properties we might want. Much of Biochemistry can be understood by looking at the functional groups present in biomolecules.

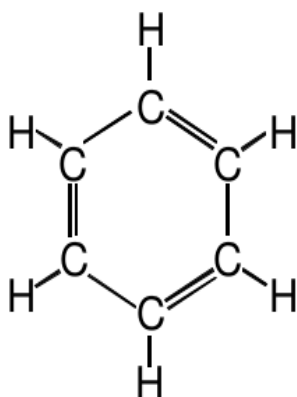
Observation 3: Molecular Structures with more than one Bonding Structure

Earlier in this concept study, we learned that different molecules can be formed from the same set of atoms. Isomers are molecules with the same molecular formula but different molecular structures, and are therefore distinctly different compounds. Rearranging the atoms in the molecule creates a new compound with new physical and chemical properties.

What if, instead of rearranging the atoms in the molecule, we rearrange the electrons? This would possibly change where double or triple bonds are located and whether there are lone pairs of electrons or not. Does this also give rise to new compounds and therefore new isomers?

We first look at benzene, a compound with the molecular formula C_6H_6 . For six carbon atoms, there are not very many hydrogen atoms. Compare benzene to hexane, which has the molecular formula C_6H_{14} . This means that there must be several double or triple carbon-carbon bonds in benzene. Experiments reveal to us two facts about the molecular structure of benzene. First, the six carbon atoms are arranged in a ring, not a chain, and each carbon atom is bonded to a single hydrogen atom. Second, the bonds between the carbon atoms in the ring all have the same length as one another. The second observation tells us that, somehow, all of the bonds in benzene are identical to each other.

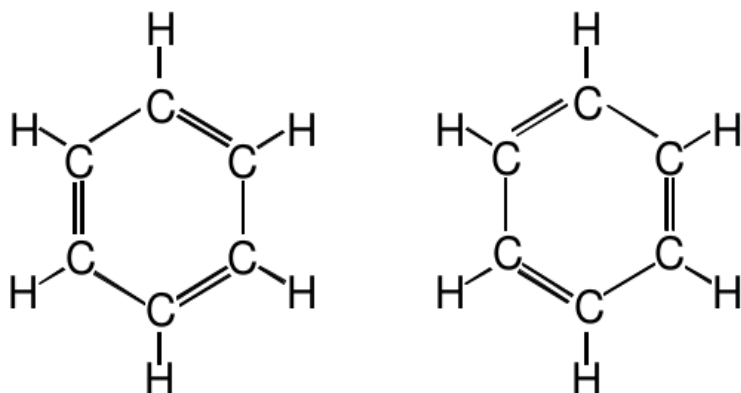
The correct molecular structure which explained these observations was a puzzle for chemists. A structure in which the six carbon atoms are arranged in a ring would be:



This structure cannot be the right structure though. Although it satisfies the octet rule and the valences of the carbon atoms, it does not correctly explain why the bonds are all the same length. This structure would predict three shorter bonds and three longer bonds.

A clue to the right structure is found from the value of the bond length, 139 pm. This length is between the typical length of a single bond, 153 pm, and the typical length of a double bond, 134 pm. This is a confusing clue: it suggests that the bonds in benzene are neither single bonds nor double bonds. We clearly need to expand on our model of Lewis structures.

If we look at the molecular structure proposed above, we can see that we made an arbitrary choice of where to put the double bonds. To satisfy the valences of the carbon atoms, we need to alternate the double bonds and single bonds, but we could have chosen the other three C-C bonds to be double:



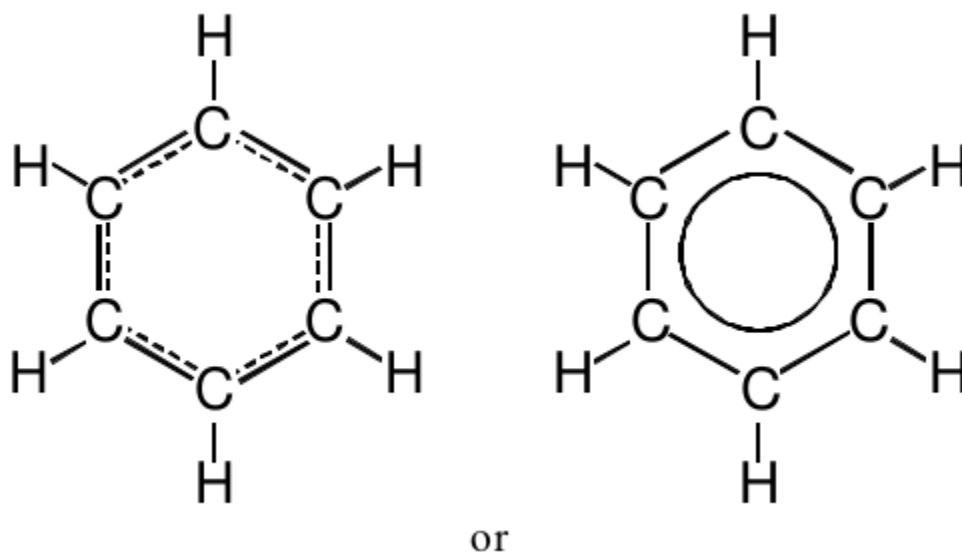
The difference between these two structures is not the arrangement of the atoms, but rather the arrangement of the electrons. Are these isomers? If they are, then there are two benzene compounds. Experimentally, we find only one. So these two structures must not be isomers. Rearranging the electrons in a molecular structure does not produce new compounds.

What then are we to do with the two structures drawn above? There is no reason why one would be preferred over the other, so both must be equally correct for benzene. But neither of them alone is correct because each of them predicts bond lengths which do not match experimental observations.

One possible answer is that there is a single molecular structure for benzene which combines both structures together. This means that the double bonds in benzene are not fixed in one set of locations or the other. Rather, the bond lengths tell us that the double bonds are spread out around the six carbon ring uniformly. The language that chemists use to describe this phenomenon is that the correct structure of benzene is a “hybrid” of the two structures drawn above. The word hybrid refers to something that contains properties of more than one element. Benzene has a single molecular structure that combines the properties of both of the above structures at the same time.

How does this explain the experimental bond lengths? If we look at each C-C bond and combine the properties of the two structures, each bond has the properties of a single bond and of a double bond. This means that the bond length would be somewhere between a single bond and a double bond, and this is just what is found experimentally.

A Lewis structure which represents this hybrid is:



The drawing on the left uses dotted lines to represent the double bonds which are neither here nor there but are rather delocalized around the six carbon ring. The drawing on the right is another way to represent this idea, but the solid ring represented the double bonds is somewhat easier to draw and therefore more commonly used by chemists. Chemists refer to the delocalization of the electrons as “resonance,” and the structure above is often called a “resonance hybrid.”

This concept applies to a number of molecules. A good example is ozone, O_3 . Experiments show that the two O-O bond lengths are equal, 128 pm. We can compare this to the double bond length in O_2 , which is 121 pm, and to the single bond length in hydrogen peroxide, H-O-O-H , which is 147 pm. From our model, we might conclude that the O-O bonds in O_3 are partially

double and partially single, just like in benzene. How would our model account for this?

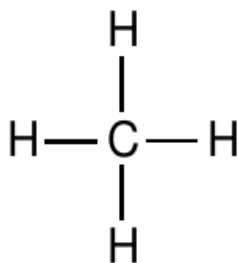
We can draw two equivalent Lewis structures for ozone:



Based on our observations and our model, we can conclude that the correct molecular structure of ozone is a resonance hybrid of these two structures in which the double bond is delocalized over both O-O bonds.

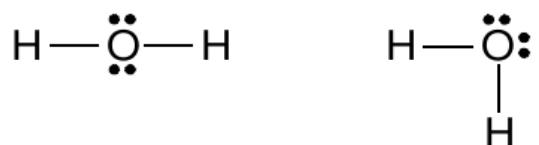
Interpretation of Lewis Structures

Before further developing our model of chemical bonding based on Lewis structures, we pause to consider the interpretation and limitations of these structures. At this point, we have observed no information regarding the geometries of molecules. For example, we have not considered the angles measured between bonds in molecules. Consequently, the Lewis structure model of chemical bonding does not at this level predict or interpret these bond angles. Therefore, although the Lewis structure of methane is drawn as

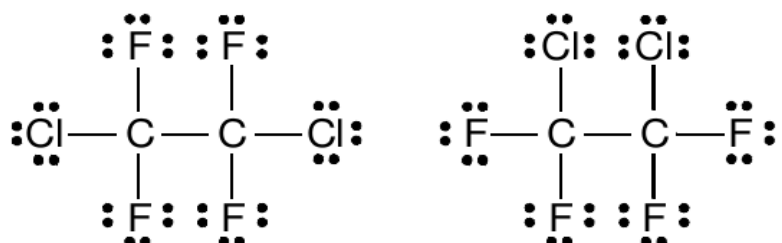


this does not imply that methane is a flat molecule, or that the angles between C-H bonds in methane are 90°. Rather, the structure simply reveals that the carbon atom has a complete octet of valence electrons in a methane

molecule, that all bonds are single bonds, and that there are no non-bonding electrons. Similarly, one can write the Lewis structure for a water molecule in two apparently different ways:



However, it is very important to realize that these two structures are identical in the Lewis model because both show that the oxygen atom has a complete octet of valence electrons, forms two single bonds with hydrogen atoms, and has two pairs of unshared electrons in its valence shell. Drawing the structure either way does not convey any different information. Neither of the structures is “more right” or “more wrong.” In the same way, the following two structures for Freon 114



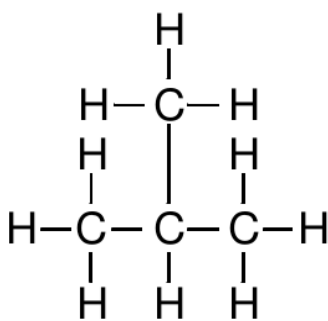
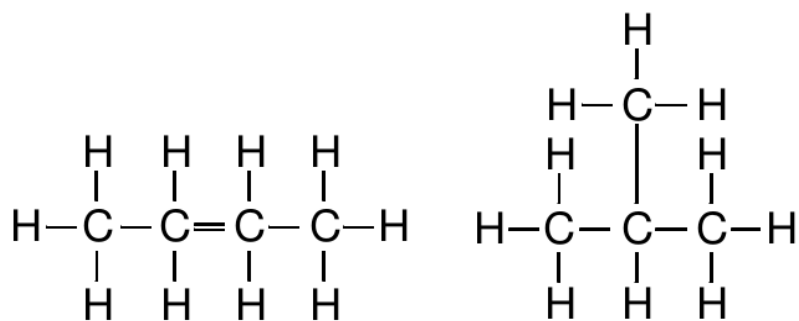
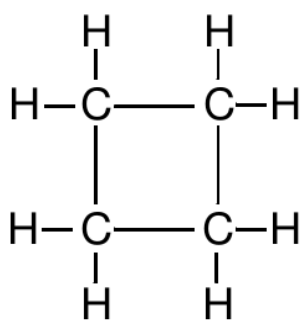
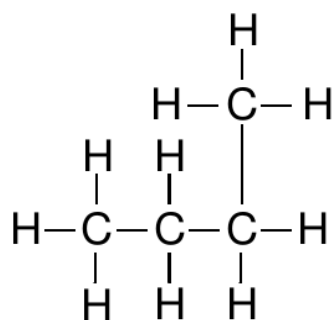
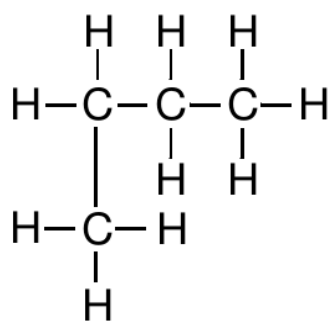
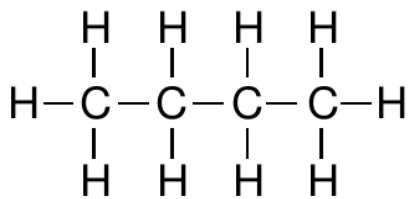
are also identical. These two drawings do not represent different structures or arrangements of the atoms in the bonds.

Finally, we must keep in mind that we have drawn Lewis structures strictly as a convenient tool for our understanding of chemical bonding and molecular stability. It is based on commonly observed trends in valence, bonding, and bond strengths. However, these structures must not be mistaken as observations themselves. As we encounter additional experimental observations, we must be prepared to adapt our Lewis

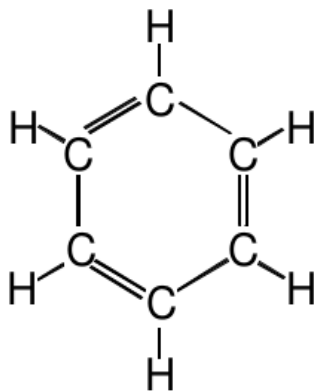
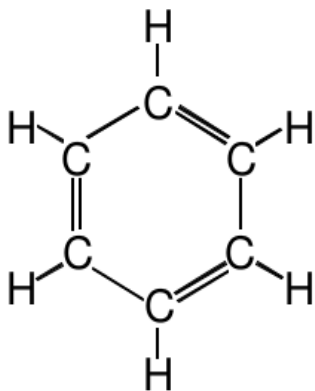
structure model to fit these observations, but we must never adapt our observations to fit the Lewis model.

Review and Discussion Questions

1. Draw molecular structures for all isomers for the molecular formula C_6H_{14} .
2. Draw Lewis structures for molecules with the molecular formula N_2O . Are these structures different isomers? Or are they resonance structures of the same molecule? How do experimental observations differ for structures which are isomers versus structures which are resonance structures?
3. A student drew the following six structures for C_4H_{10} . Which of these are correct structures? Of the correct structures, which are identical and which are isomers? Are any of the structures resonance structures?



4. We drew two benzene structures with alternating double bonds as follows:



It looks like the structure on the right is simply a 60° rotation of the structure on the left. Viewed this way, it might seem that these two are the same structure and the correct structure of benzene is just one of these. Provide experimental evidence and reasoning to demonstrate that this is not the correct interpretation of these two Lewis structures.

5. Amino acids are small molecules which link together in long chains to form proteins. The name “amino acid” comes from the fact that each molecule contains an amine group and a carboxylic acid group (see the table of functional groups in this study.) The amino acid alanine has molecular formula $\text{C}_3\text{H}_7\text{NO}_2$. Given that it is called an amino acid, use the table to draw a molecular structure for alanine.

Energy and Polarity of Covalent Chemical Bonds

Introduction

The Lewis model of chemical bonding is one of the most powerful models in all of Chemistry. With the simple concepts of the octet rule and the sharing of an electron pair to form a chemical bond, we can predict what combinations of atoms and which molecular structures are likely to be stable or unstable. For example, we can predict that the molecular formula C_4H_{10} should correspond to a stable molecular structure, since it is possible to draw a Lewis structure in which all four carbon atoms have an octet of valence electrons and each hydrogen atom has two valence electrons. In fact, we can even predict that there should be two such molecular structures corresponding to two different stable compounds, butane and methyl propane (often called isobutane). Lewis structures also allow us to predict the relative strengths and lengths of chemical bonds. For example, we can predict that in the molecule propene C_3H_6 , one of the C-C bonds is a single bond and the other is a double bond; correspondingly, we can predict that the double bond is shorter and stronger than the single bond.

In general, for any molecule containing some combination of atoms of C, N, H, O, and any of the halogens (F, Cl, Br, or I), we can predict with confidence that the molecule will be a stable compound if we can draw a Lewis structure in which the C, N, O, and halogen atoms all have an octet of valence electrons. This is a very significant statement, since the overwhelming majority of the molecules of organic chemistry are composed of only these atoms. The converse is also generally true: if we cannot draw a Lewis structure in which these atoms have an octet of valence electrons, we will predict fairly confidently that a stable compound of that molecular formula probably does not exist. Note that “stable” does not mean “non-reactive.” In this context, “stable” means that the compound exists and can be isolated for long periods of time. Methane CH_4 is a stable compound which can be manufactured, captured, stored, and transported. However, it is also a reactive compound, reacting rapidly with oxygen gas in one of the most common combustion reactions in the world.

These are the reasons why we say that the Lewis structure model of covalent bonding is one of the most important models in all of Chemistry. However, like most good models, the understanding we get from the model comes with even more questions we might want to ask. In this Concept Development Study, we will address several of these, while others will wait for later studies. First, why does sharing a pair of electrons create a chemical bonding? More pointedly, what does it even mean to “share” an electron between two atoms? And why do atoms prefer to share a pair of electrons, rather than one or three? Of course, we’ve also seen that atoms can share more than one pair of electrons, creating double or triple bonds. We might have guessed that, with more electrons being shared, these electrons would repel each other, leading to a higher energy, but this is not the case. Why does sharing more than one pair of electrons produce a stronger bond?

Once we have an understanding of what sharing electrons means, we will also ask whether the atoms really do “share” these electrons fully. We already know that the energies of electrons in different atoms are quite different. We have observed and analyzed the ionization energies of electrons in atoms. These results showed that the electrons in some atoms such as fluorine, for example, are much more strongly attracted to their nuclei than in atoms such as carbon, for example. Knowing this, we might readily ask whether the electrons shared by a C atom bonded to an F atom are actually shared equally. If they are not equally shared, does it matter? Does this affect the physical or chemical properties of the molecules?

As always, we will examine experimental observations to help us understand the answers to these questions.

Foundation

In this Concept Development Study, we will assume that we already know the basic rules of the Lewis model of chemical bonding. Chemical bonds between atoms consist of one, two, or three pairs of shared electrons, respectively resulting in single, double, or triple bonds. Atoms in groups IV, V, VI, and VII, most importantly including C, N, O, and F, share electrons in pairs such that, in stable molecules, these atoms typically have eight

electrons in their valence shells. An H atom will share one pair of electrons with other types of atoms to form stable molecules.

We will need Coulomb's Law to understand how the bonding electrons interact with the nuclei of the atoms that share them. We have already used Coulomb's Law to understand the energies of electrons in atoms and how these vary from one type of atom to another. These same lines of reasoning will be useful for electrons in molecules.

Though we will not need all of the postulates and conclusions of Quantum Mechanics, there are a few that we will call on to answer the questions posed above. This makes sense, since any discussion of where electrons might be found or how they might move certainly requires us to take a quantum mechanical view of electrons. Most notably, we'll need to recall that the motion of electron is described by an "orbital" which provides the probability for where the electron might be. In addition, we'll recall that an electron can exist in two different "spin states," and that two electrons' motions may be described by the same orbital only if they have different spin states.

Observation 1: The Simplest Chemical Bond, H_2^+

Let's start with the easiest molecule we can imagine. We need at least two atoms of course, so that means we need two nuclei. The smallest nucleus is just a single proton, in other words, a hydrogen ion, H^+ . We could try to build a molecule formed from just two of these, but this seems unlikely. The two positively charged nuclei would just repel each other, so there can't be such a molecule. We need at least one electron to provide some attraction. Is one enough? The best way to answer that question is to ask whether the combination of two H^+ nuclei plus one electron is a stable molecule, H_2^+ .

Experimentally, it is indeed possible to observe H_2^+ . Even though it is far less common than H_2 , it does exist. What does this mean in terms of chemical bonding? It means that H_2^+ does not spontaneously fall apart into an H atom and an H^+ ion. Instead, to break the bond we would have to do some work, or, in other words, add some energy. This amount of energy can be measured and is 269 kJ/mol. That is actually quite a lot of energy which

must be added to pull an H atom and an H^+ ion apart, so a strong bond is formed when the two H^+ nuclei share a single electron. This might seem surprising, since our model of chemical bonding based on Lewis structures regards a chemical bond as a sharing of a pair of electrons. We'll examine the importance of sharing two electrons instead of one in the next section.

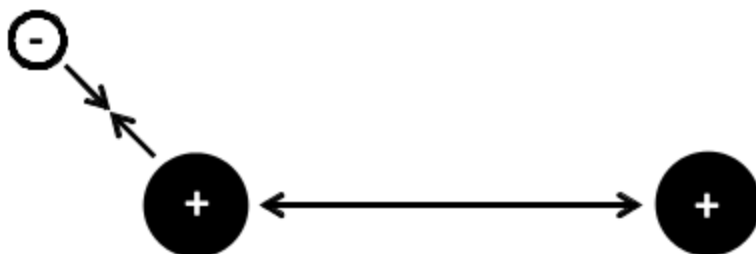
But first, let's ask why sharing an electron creates a bond. A better way to ask this question would be why is the energy of the electron lower when the electron is shared by two nuclei instead of being near to only one? We know that an electron and a proton attract each other via Coulomb's law, and the closer the two are, the lower the energy. As such, if an electron can be attracted to two protons, it has a lower energy even if the two protons are not next to each other. This is illustrated in [\[link\]](#)b, which shows the attraction of the electron to both nuclei as well as the repulsion between the two nuclei. When the electron is near to two nuclei, it has a lower potential energy than when near to only one because its attraction to a second positively charged nucleus further lowers its energy.

We can rearrange the electron and the two nuclei, such that the electron is on the "outside" of the molecule ([\[link\]](#)a). Here, it is close to one nucleus but not the other. In this case, the repulsion of the two nuclei is greater than the attraction of the electron to the distant nucleus. Just using Coulomb's law, the energy of the electron in this position is slightly lower than when it is on one nucleus, but the repulsion of the nuclei is large.

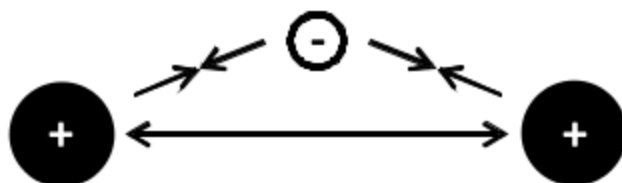
From a comparison of the arrangements of the electron and the two nuclei, it appears that we get a lowering of energy when the electron is "between" the two nuclei and not otherwise. This suggests what "sharing an electron" means when forming a chemical bond. Since the shared electron has a lower energy, we would have to raise the electron's energy to pull the two nuclei away from each other.

Now we know why a chemical bond is formed when two atoms share at least one electron. The energy of the electron is lower when shared in the molecule than it is in the separated atoms because it is attracted to both positive nuclei at the same time. To break the bond formed by sharing the electron, we must do work, which means we have to add energy to raise the energy of the electron to be able separate the atoms.

Attractions and Repulsions in H_2^+



- (a) When the electron is outside of the region between the two nuclei, the repulsion of the nuclei exceeds the attraction of the electron to the nuclei, and no bonding force is expected.



- (b) When the electron is in the region between the two nuclei, the attraction of the electron to the two nuclei exceeds the repulsion of the nuclei, lowering the total energy of the molecule and producing bonding.

Attractions and Repulsions in H_2^+

For now, we should make a note to ourselves that all of this discussion of electron energy includes only a discussion of potential energy. It also assumes that the electron is at some particular location where we can calculate its potential energy. This ignores the uncertainty principle of quantum mechanics, suggesting that the model is not physically accurate. Both of these issues need to be corrected, so we need a better understanding of the sharing of electrons in chemical bonds.

Observation 2: The Simplest Molecule, H₂

The hydrogen molecule is familiar to us from our early efforts to determine molecular formulae. Avogadro was the first person to suggest that hydrogen gas consists of diatomic molecules, H₂, instead of individual hydrogen atoms. This was a perplexing idea for the chemists of the early nineteenth century. Why would identical H atoms be attracted to each other? Of course, they did not know anything about the structure of these atoms, including that each atom contains a positive nucleus and an electron. From our work on H₂⁺, we now have a clue as to what holds the two H atoms together. It must be electron sharing.

What observation can we make about the bonding in H₂? Clearly, it is a stable molecule. Although H₂ molecules are highly reactive, they do not spontaneously fall apart into H atoms except under very extreme circumstances. Experimental data tell us that the bond energy of H₂ is 436 kJ/mol. This is even more energy than is required to break the bond in H₂⁺, nearly twice as much in fact. Remember that to break the bond in H₂⁺ we must raise the energy of the shared electron. Perhaps, in H₂, we have to raise the energy of the two electrons, costing us about twice the energy. This seems to be a good starting point for understanding the strong bond in H₂.

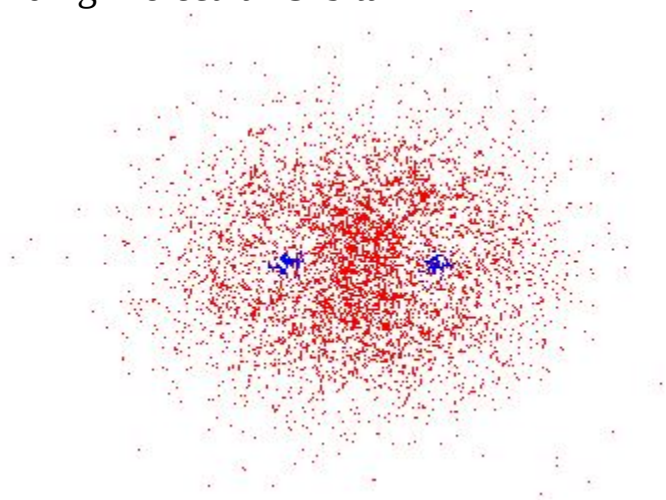
But there are some troubling questions about this simple picture. This model would suggest that sharing more than two electrons should give an even greater bond energy. But this is only true for some molecules, and it is certainly not true for H₂. There is something significant about sharing a pair of electrons, rather than one or three. In addition, the strength of the bond (436 kJ/mol) is actually less than double the strength of the bond with one shared electron (269 kJ/mol). There must be another factor at work. And finally, there are the questions we ended with in the last section: what about kinetic energy? And what about the uncertainty principle, which states that an electron is not actually localized?

Let's work our way backwards through these questions. We know from our study of quantum mechanics that the motion of an electron is described by an "orbital" which provides the probability for where the electron might be found. We can't actually know where an electron is, but we can look at its

probability distribution. This is true for electrons in molecules just like it is in atoms. We just need to observe what an orbital looks like for an electron that is shared by two nuclei.

Such a “molecular orbital” for the electron in H_2^+ is shown in [\[link\]](#). We’ve seen images like this when we discussed atomic orbitals. Remember that this image of a cloud gives us a probability: where there are many dots, the probability is high. The electron can be found near either nucleus but can also be found with high probability in the area between the two nuclei. This seems encouraging when thinking about the energy of the electron in the molecule as we discussed in the previous section. When the electron is in the region between the two nuclei, the potential energy of the electron is lower.

Bonding Molecular Orbital



orbital image courtesy of M. Winter, “The Orbitron” website
(<http://winter.group.shef.ac.uk/orbitron/>)

There is a second interesting aspect to the molecular orbital. It is larger in space than the atomic orbital that the electron would occupy if it were in a single H atom. Why does this matter? Thinking back to our study of the energies of electrons in atomic orbitals, we can recall that both potential energy and kinetic energy are important. The kinetic energy of the electron

is easiest to understand by remembering the uncertainty principle. The more the electron is confined, the less certain is its momentum. This means that, on average, the electron moves faster with greater kinetic energy when it is confined to a smaller space. When less confined, the electron can have lower kinetic energy. Since the molecular orbital confines the electron less than the atomic orbital does, the kinetic energy of the electron is lower in the molecular orbital than it is in the atomic orbital. (Some very complicated calculations show that this fact is the single most important factor in lowering the energy of the electron in a bond. For simplicity, we will assume that both lower potential energy and lower kinetic energy contribute to the strength of a chemical bond.)

[\[link\]](#) shows a molecular orbital for H_2^+ . However, we were discussing the bond strength in H_2 and, in particular, the fact that two electrons seem to be better than one. Again, we have to refer back to our study of the quantum energy levels and electron configurations of atoms. Remember that there were rules from both quantum and experimental observations which restrict what energy states electrons can occupy. Most importantly, there is an important aspect about two electrons: only two electrons can occupy a single orbital. As a very good model then, we can imagine that the two electrons in H_2 both move as described by the probability in the molecular orbital in [\[link\]](#). This means that both electrons have their energy lowered, just as the single electron has its energy lower in H_2^+ . This means that, to separate the two H atoms, it takes more energy to raise the energies of these two electrons than to raise the energy of just one. So the bond energy of H_2 is much greater than the bond energy of H_2^+ .

From quantum mechanics, we can't add a third electron to this molecular orbital. We don't need the detail now to know what would happen if we added a third electron to an H_2 molecule, but we can say that the energy of the third electron is not lowered. The strongest bond is formed by sharing just two electrons, not more and not less.

And finally, why is the bond energy of H_2 not double the bond energy of H_2^+ ? With two electrons in the same orbital, it would seem that we need double the energy of one electron to separate the atoms. Of course, this would assume that the two electrons are unaffected by each other, with

energies which do not depend on each other. This can't be true, since two electrons will repel each other by Coulomb's Law. In an atomic orbital, we saw that electron-electron repulsion raised the energy of both electrons sharing an orbital. The same is true in a molecular orbital. This means that the energy of each electron in H_2 is not the same as the energy of the one electron in H_2^+ . In a discussion question, we consider the question of why this means that the bond energy in H_2 is less than double the bond energy in H_2^+ .

Observation 3: Dipole moments in Diatomic Molecules

We now have an understanding of what it means for two atoms to share an electron pair and why this results in a bond. In addition to H_2 , this description works well in describing and understanding chemical bonds such as in F_2 or Cl_2 . More work is required to understand multiple bonds such as the double bond in O_2 , but it turns out that the same principles apply. What about molecules where the atoms are not the same, e.g. HF ? The Lewis model of these molecules still assumes a sharing of an electron pair. But we learned in our study of atomic structure that the properties of H atoms and F atoms are quite different. For example, the ionization energy of an F atom is larger than the ionization energy of an H atom. F atoms also have very strong electron affinity. Do such different types of atoms share electrons? If so, does it matter that the properties of the two atoms are so different?

We need observations to answer these questions. First, we can do as we did with H_2 and examine the energies of the bonds between different atoms. The bond energy of HF is 568 kJ/mol, larger than the bond energy of H_2 . By contrast, the bond energy of F_2 is 154 kJ/mol, quite a bit weaker than the bonds in either HF or H_2 . The bond energy of HCl is 432 kJ/mol, weaker than the HF bond. The energy of one O-H bond in H_2O is 463 kJ/mol. Clearly, the strength of bond depends on what types of atoms are bonded together. This suggests that the sharing of an electron pair depends on the properties of the atoms in the bond, including the sizes of the atoms and the charges on the nuclei. In fact, it would not be too surprising if different atoms did not share the electrons equally.

To find out if this is the case, we observe a property of molecules called the “dipole moment.” An electric dipole is simply a separation of a positive and a negative charge. The dipole moment, usually labeled μ , measures how strong the dipole is by taking the product of the amount of the charge times the separation of the charge. Just having a positive charge, let’s say a proton, and a negative charge, let’s say an electron, does not mean that there is a dipole moment. The hydrogen atom does not have a dipole moment because the electron is in constant rapid motion around the positive nucleus. As such, viewed from outside the atom, there is no positive “end” or negative “end” to the hydrogen atom, so there is no dipole moment. This is true of all atoms.

It might seem that molecules could not have dipole moments for the same reason. The electrons are moving about the nuclei rapidly. In the H_2 molecule, although there are positive and negative charges, there is no end of the molecule which looks more positive and no end which looks more negative. H_2 does not have a dipole moment.

What about a molecule like HF? If an H atom has no dipole moment and an F atom has no dipole moment, does HF have a dipole moment?

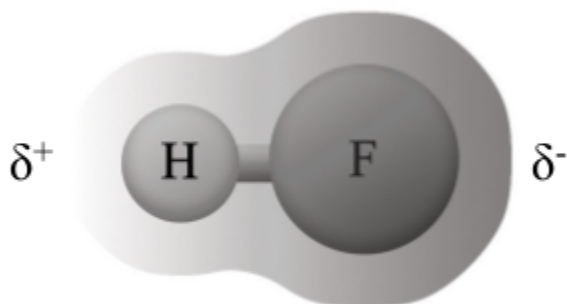
Experimentally, molecular dipoles can be observed in a number of ways. If you put a molecule with a dipole moment in an electric field, it will line up with the field, with the positive end of the dipole pointed towards the negative end of the field. Dipoles can interact with each other as well, so that the negative end of one dipole will point towards the positive end of another dipole.

It is also possible to measure the magnitude of the dipole moment. A number of these are given in [\[link\]](#) for some simple molecules. We can see that, not only does HF have a dipole moment, but in fact it has the largest dipole moment of the molecules listed. What does it mean that HF has a dipole moment? An HF molecule must have a permanent negative end and a permanent positive end. Experimentation shows that the F end of the molecule has a net negative charge and the H end has a net positive charge.

Molecule	μ (debye)
H ₂ O	1.85
HF	1.91
HCl	1.08
HBr	0.80
HI	0.42
CO	0.12
CO ₂	0
NH ₃	1.47
PH ₃	0.58
AsH ₃	0.20
CH ₄	0
NaCl	9.00

Dipole Moments of Specific Molecules

How can this be so? The total number of electrons and protons in the molecule are evenly matched, of course, and the electrons are moving rapidly about the two nuclei just as in H₂. Perhaps the electrons are not moving uniformly around the H and the F nuclei. To observe this, we look at the molecular orbital for the shared electrons in the HF bond, shown in [\[link\]](#).

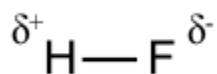


Distribution of Electron Probability in HF

We observe that the electrons in the molecule move with greater probability near the F atom. There is thus more electron charge around the F nucleus than the positive charge on the F nucleus. And the opposite is true for the H end of the molecule. Apparently, when an H atom and an F atom share electrons, they do not share them equally!

This is an extremely important result, one of the most useful in all of Chemistry. Different atoms have different tendencies to draw electrons to themselves when sharing electrons in a covalent bond. The relative strength with which an atom draws electrons to itself in a bond is called “electronegativity.” A very electronegative atom will attract the shared electrons more strongly than a less electronegative atom. This will produce a negative charge near the more electronegative atom and a positive charge near the atom other. This will, in most cases, create a permanent dipole moment in the molecule. At this point, we don’t know how much negative charge is near the more electronegative atom, but it probably is not the full charge on a single electron since the electrons are still mostly shared by the two atoms. As such, we label the negative charge by δ^- , where δ is some number between 0 and 1. In most cases, we don’t even need to know how large δ is. The positive end of the molecule is labeled by δ^+ , since whatever the negative charge on the negative end must equal the positive charge on the positive end. HF is a good starting example. The F atom is more

electronegative than the H atom; hence, the HF molecule has a dipole moment, which makes HF what we call a polar molecule.



Of course, we next want to know why the F atom is more electronegative. We need more data to develop a model for electronegativity. [\[link\]](#) listing the dipole moments of several molecules provides good data for comparison.

Let's first study the set of molecules HF, HCl, HBr, and HI. It is easy to see that the dipole moments of these molecules are in the order of $\text{HF} > \text{HCl} > \text{HBr} > \text{HI}$. To analyze this comparison, we need to remember that the dipole moment measures the product of the amount of charge separated times the distance by which the charges are separated. Since the dipole moment of HF is larger than that of HCl, let's compare these two. How do the properties of F atoms compare to those of Cl atoms? One thing we can say for sure: Cl is a larger atom than F. This means that the HCl bond (127 pm) is longer than the HF bond (92 pm). Since the dipole moment depends on the distance between the positive and negative charges, the comparison of bond lengths would perhaps lead us to predict that HCl would have a larger dipole moment than HF. But that's not what the data tell us. There is only one way to explain this. The difference between HF and HCl must be in the amount of charge that is separated. It must be true that the negative charge on the F atom is greater than the negative charge on the Cl atom. This means that F attracts the shared electrons in the H-F bond more than the Cl atom attracts the shared electrons in the H-Cl bond. This means that F is more electronegative than Cl.

Looking at the dipole moments of these four molecules and remembering that the atoms get larger in the order $\text{F} < \text{Cl} < \text{Br} < \text{I}$, it must be true that the electronegativities go in the order $\text{F} > \text{Cl} > \text{Br} > \text{I}$. In this group, the electronegativity is larger for smaller atoms. To see if this turns out to be generally true, we can examine other families in the periodic table.

First, let's look at the dipole moments for H_2O and H_2S . H_2O has a dipole moment with the O being the negative end. This means that O is more electronegative than H. H_2S also has a dipole moment, but it is much smaller than that of H_2O , so S is less electronegative than O. Let's compare the dipole moments of NH_3 and PH_3 : we see the same trend. It is generally true that electronegativity is larger for smaller atoms.

We should also compare the electronegativities of elements in the same row of the Periodic Table. For example, the dipole moments increase in the order of $\text{NH}_3 < \text{H}_2\text{O} < \text{HF}$, and $\text{PH}_3 < \text{H}_2\text{S} < \text{HCl}$. From this, we can conclude that, in general, electronegativity increases with increasing atomic number within a single row of the Periodic Table.

Electronegativity is an extremely useful concept in chemistry, but it is not a precisely defined physical property. In fact, there are several possible definitions of how to measure electronegativity each of which leads to slightly different values for each atom. Although the exact values vary, the overall trends we observed are similar. Using one popular definition, [\[link\]](#) shows electronegativities for many atoms. Looking at these numbers, you should be able to see the trends we have developed from analyzing dipole moments of simple molecules.

Atom	Electronegativity (X)
H	2.1
He	-
Li	1.0
Be	1.5

Atom	Electronegativity (X)
B	2.0
C	2.5
N	3.0
O	3.5
F	4.0
Ne	-
Na	0.9
Mg	1.2
Al	1.5
Si	1.8
P	2.1
S	2.5
Cl	3.0
Ar	-
K	0.8
Ca	1.0

Electronegativity of Selected Atoms

With these observations in mind, we need to develop a model to understand why the electronegativity is larger for a larger atomic number in a single row, but is smaller for a larger atomic number in a single group. These trends seem to contradict each other. There must be a good physical explanation of these observations.

To find one, let's note that both trends point to F being the most electronegative element. F is as far to the right on the table as we can go and as far to the top of the table as we can go. (We might consider He or Ne to be more electronegative, but since there are no known molecules containing bonds with He or Ne, electronegativity has no meaning for these atoms.) What else do we know about F atoms? Thinking back on our understanding of atomic energy levels, we recall that F atoms have the highest ionization energy (except for He and Ne) and the highest electron affinity of any of the elements. Electrons are clearly most strongly attracted to F atoms. We developed a model to explain this based on Coulomb's law. The F atom uniquely combines the largest "core" charge and the smallest distance of the valence electrons to the nucleus (measured as the average orbital distance). Perhaps these two factors are also responsible for F having the largest electronegativity.

To find out, we should examine other elements with high electronegativities. The highest electronegativities are all for elements with high ionization energies. Interesting examples include N, O, and Cl. Of these, O has the highest electronegativity, and this makes sense: it has a large core charge and a small shell radius. But if we compare N and O, N has the higher ionization energy. There must be more to electronegativity than just ionization energy. Another interesting comparison of N and O is that N has no electron affinity whereas O has a strong electron affinity, so electron affinity must also be important in understanding electronegativity. This makes sense: an atom with a higher ionization energy is less likely to have its electrons drawn to another atom in a chemical bond, and an atom with a higher electron affinity is more likely to draw electrons from another atom in a chemical bond.

This produces a simple model to understand electronegativity. Atoms with higher ionization energies and higher electron affinities have higher

electronegativity. The reasons for high ionization energy and high electron affinity are the same as the reasons for high electronegativity. On the basis of Coulomb's law, a larger core charge and a smaller shell radius generally give larger ionization energy, larger electron affinity, and larger electronegativity. One way to define electronegativity is simply as the average of the ionization energy and the electron affinity. In fact, the values in [\[link\]](#) are just this average multiplied by a constant to give a simplified scale.

Understanding these trends is extremely useful. Electronegativity is one of the most powerful concepts in chemistry for predicting chemical reactivity. For example, positive ends of molecules are often attracted to the negative ends of other molecules. Understanding where there may be a more negative charge in a molecule can then help us predict the location in a molecule where a reaction may take place or even predict whether a reaction is expected to occur or not. We will have many occasions to apply the concept of electronegativity, including in the next concept study.

Review and Discussion Questions

1. Why does an electron shared by two nuclei have a lower potential energy than an electron on a single atom? Why does an electron shared by two nuclei have a lower kinetic energy than an electron on a single atom? How does this sharing result in a stable molecule? How can this affect be measured experimentally?
2. The bond in an H_2 molecule is almost twice as strong as the bond in the H_2^+ ion. Explain why the H_2 bond is so much stronger. Why isn't the H_2 bond exactly twice as strong as the H_2^+ bond?
3. The ionization energy of H_2 is slightly less than the ionization energy of H_2^+ . But the bond energy of H_2 is much larger than the bond energy of H_2^+ . Explain how these two facts are consistent with each other.
4. In this study, we referred to H_2 as a "stable" molecule. But H_2 gas can be explosively reactive, as a viewing of the Hindenberg disaster clearly reveals. In what sense is H_2 "stable?" How can a stable molecule be a highly reactive molecule?
5. Explain why an atom with a high ionization energy is expected to have a high electronegativity.

6. Explain why an atom with a high electron affinity is expected to have a high electronegativity.
7. Explain why S has a greater electronegativity than P but a smaller electronegativity than O.
8. N atoms have a high electronegativity. However, N atoms have no electron affinity, meaning that N atoms do not attract electrons. Explain how and why these facts are not inconsistent.

Bonding in Metals and Metal-Non-Metal Salts

Introduction

We have noted that the Lewis model of chemical bonding is very powerful in predicting structures, stability, and reactivity of molecules. But there is a glaring hole in our model that you may have noticed: the metal elements are missing. Additionally, the Lewis model only applies to a handful of atoms at a time, and we have not examined what happens in solids that have huge numbers of atoms bonded in vast networks.

The Lewis model is based on the “octet rule” and the concept of a covalent bond as a sharing of an electron pair. These were developed based on the molecules formed by elements in Groups 4 to 8, and most specifically, the group of elements we call the “non-metals.” This name clearly says that the properties of the non-metal elements are very different from the properties of metal elements. We will look at these differences in this study. But even without analyzing those differences, we can say immediately that the octet rule does not seem to apply to these elements. Remember that the octet rule says that the number of valence electrons plus the valence of the atom (the number of bonds the atom typically forms) commonly equals 8 for compounds formed by the non-metal elements. Rather than being the general rule for metals, this is very rarely true. This means that we need a new model for bonding in metals and in compounds that contain metal atoms.

To develop this model, we will examine the specific properties of metallic elements, which differ significantly from the non-metals. By considering these properties carefully, we will be able to build a model which accounts for these properties.

Of course, to be more complete, we also need to consider compounds formed from combinations of metal atoms and non-metal atoms. These also have properties which differ greatly from either metals or non-metals. Again, by looking closely at these properties, we will be able to build a model for metal-non-metal bonding, which is different from that in metal bonding.

This means that we will develop models of two new types of bonding in addition to the one we have already developed for covalent bonding. It would be very helpful to find a way to tie these three types of bonding together, to give a simple understanding of why the bonding is different for different types and combinations of atoms. In the last section of this study, we will create such a model based on our understanding of the chemical concept of “electronegativity,” developed in the previous concept study.

Foundation

In this study, we will assume that we know the essential components of the structure and properties of individual atoms. Each atom has an electronic configuration which determines its physical and chemical properties, including ionization energy, electron affinity, atomic size, and electronegativity. Electron motion is described by orbitals, which give the probability for the electron in space around the nucleus. The energy of each electron is determined by a combination of its kinetic energy, its attraction to the nucleus, and its repulsion from other electrons in the atom. Our model considers the electron-electron repulsion as a “shielding” of the positive charge of the nucleus, resulting in an effective nuclear charge which is less than the actual nuclear charge, which we refer to as the core charge. By looking at the core charge experienced by an electron in an atom and at its distance from the nucleus, we can understand the ionization energy of that electron. We know and can account for the fact that the ionization energies are greatest for atoms near the right side of the periodic table with large core charges. And the ionization energies are greater for smaller atoms, where the valence electrons are closer to the nucleus.

In a previous study, we developed the concept of electronegativity. An atom with a high electronegativity strongly attracts the shared electrons to itself in a covalent bond. The atom with the lower electronegativity in the bond more weakly attracts the shared electrons. The result is that the bond is “polar,” meaning that one end of the bond is negatively charged and the other end is positively charged. We will assume a previous understanding of the variations of electronegativity amongst the elements. Atoms to the right in the Periodic table have higher electronegativities than those to the left. And atoms in the earlier rows of the Periodic Table have higher

electronegativities than those in the later rows. Electronegativity thus generally increases from “left to right” and “down to up” in the Periodic Table. These facts will be extremely useful in understanding how and why different types and combinations of atoms form different types of bonds.

Observation 1: Properties of Metals

Historically, people have worked to locate, isolate, and purify metals because of their valuable properties. Most metals are both strong and malleable solids, meaning that they can be shaped, bent, pressed, flattened, and so forth without cracking or breaking. This is a very useful property. Shelters, shields, tools, and armor can be made from solids provided that they can be bent to whatever shape is desired. Since they are not brittle, metals do not break on impact so they provide excellent protection as well as excellent materials for weapons.

In the age of electricity, many metals became more valuable due to their conductivity. When a piece of metal is bridged across an electric potential, electrons flow from the negative electrode to the positive electrode, creating a current with obvious applications. By contrast, non-metals are rarely conductors and are more typically insulators. Adding to the applications of metals for electricity, metals are also ductile, meaning that they can be drawn into thin wires while maintaining strength.

And not least, most metals are actually quite attractive, with shiny, smooth, colorful finishes. This gives metals intrinsic value in addition to their usefulness. It is not surprising that gold, silver, and copper have long been used for coins and jewelry, given their beauty and their resistance to oxidation.

We can examine these properties of metals to try to understand how metal atoms are bonded together. The distinct properties of metals tells us that the bonding must be quite different from that in the covalent molecules of the non-metals we have been studying so far. These differences must relate to the differences in the properties of the individual atoms. So let's take a look at those properties.

Perhaps the most important atomic property is, as we often have seen, the ionization energy of each metal atom. [\[link\]](#) shows the first ionization energy for each atom in the third and fourth rows of the Periodic Table, including both metals and non-metals. What trends do we see in these data? Two trends appear very clearly. One trend is that the ionization energies of metals are significantly lower than the ionization energies of the non-metals. Another trend is that the ionization energies of the metals do not vary much from metal to metal. This is very different from the sharp increases we see in the non-metals as we move across the periodic table.

Element	Atomic Number (Z)	First Ionization Energy (kJ/mol)
Na	11	495.85
Mg	12	737.76
Al	13	577.54
Si	14	786.52
P	15	1011.82
S	16	999.60
Cl	17	1251.20
Ar	18	1520.58
K	19	418.81
Ca	20	589.83

Element	Atomic Number (Z)	First Ionization Energy (kJ/mol)
Sc	21	633.09
Ti	22	658.82
V	23	650.92
Cr	24	652.87
Mn	25	717.28
Fe	26	762.47
Co	27	760.41
Ni	28	737.13
Cu	29	745.49
Zn	30	906.41
Ga	31	578.85
Ge	32	762.18
As	33	944.46
Se	34	940.97
Br	35	1139.87
Kr	36	1350.77

Ionization Energies of Different Elements

We have already discussed the first trend in our study of atomic structure. We explained the lower ionization energies for metals compared to non-metals from the fact that the metals have relatively lower core charges. In our previous studies, we saw that the core charge increases for atoms as we increase the atomic number in a single row of the Periodic Table. Each row consists of elements with valence electrons in the same energy shell. The metals are more “to the left” in each row, meaning that they have smaller core charges for that row. This explains the relatively lower ionization energies.

The lack of big variations in the ionization energies of metals is harder to understand. We have seen that the ionization energy of an atom is determined by the electron configuration. For the metal atoms, these electron configurations are a little trickier than for the non-metals. These are illustrated in [\[link\]](#) for the atoms in the fourth row of the Periodic Table, beginning with K. In each of these atoms, the 4s and 3d subshells have energies which are very close together. In K and Ca, the 4s orbital energy is lower, so the outermost electron or electrons in these two atoms are in the 4s orbital and there are no 3d electrons. For the transition metal atoms from V to Cu, these atoms have both 4s and 3d electrons and the number in each orbital depends very sensitively on exactly how many valence electrons there are and what the core charge is. As such, the actual electron configurations in [\[link\]](#) would have been very hard to predict and we will treat them as data which we have observed.

K	$[\text{Ar}]4s^1$
Ca	$[\text{Ar}]4s^2$
Sc	$[\text{Ar}]3d^14s^2$
Ti	$[\text{Ar}]3d^24s^2$

K	$[\text{Ar}]4s^1$
V	$[\text{Ar}]3d^34s^2$
Cr	$[\text{Ar}]3d^54s^1$
Mn	$[\text{Ar}]3d^54s^2$
Fe	$[\text{Ar}]3d^64s^2$
Co	$[\text{Ar}]3d^74s^2$
Ni	$[\text{Ar}]3d^84s^2$
Cu	$[\text{Ar}]3d^{10}4s^1$
Zn	$[\text{Ar}]3d^{10}4s^2$
Ga	$[\text{Ar}]3d^{10}4s^24p^1$
Ge	$[\text{Ar}]3d^{10}4s^24p^2$
As	$[\text{Ar}]3d^{10}4s^24p^3$
Se	$[\text{Ar}]3d^{10}4s^24p^4$
Br	$[\text{Ar}]3d^{10}4s^24p^5$
Kr	$[\text{Ar}]3d^{10}4s^24p^6$

Electron Configurations of Period 4 Elements

A clear and surprising rule in the data in [\[link\]](#) is that the outermost electron in each atom is always a 4s electron. As we increase the atomic number from V to Cu, there are more 3d electrons, but these are not the highest energy electrons in these atoms. Instead, these added 3d electrons increasingly shield the 4s electrons from the larger nuclear charge. The

result is that there is not much increase in the core charge, so there is not much increase in the ionization energy, even with larger nuclear charge.

This model explains the data in [\[link\]](#). Although this analysis probably seems complicated, it helps us to understand the important observation that all of the metals have low ionization energies.

How do these electron configurations determine the properties of metals? Or stated more specifically, how do the electrons configurations affect the bonding of metal atoms to each other, and how does this bonding determine the properties of the metals? To find out, let's look at each property and develop a model that accounts for it. First, think about the electrical conductivity of metals. When a relatively low electric potential is applied across a piece of metal, we observe a current, which is the movement of electrons through the metal from the negative to the positive end of the electric field. The electrons in the metal respond fairly easily to that potential. For this to happen, at least some of the electrons in the metal must not be strongly attracted to their nuclei. Does this mean that they are somewhat "loose" in the metal? In fact, we have seen that this is true: the ionization energy of metal atoms is low. Perhaps the valence electrons are somewhat "loose" in the metal. A metal's conductivity tells us that when we have many metal atoms (let's say 1 mole, for example), there are electrons available to contribute to the current when an electric potential is applied. Thus, the valence electrons must not be localized to individual nuclei but rather are free to move about many nuclei.

Second, let's think about the malleability and ductility of solid metals. These properties mean that the bonding of the metal atoms together is not affected much when the atoms are rearranged. It may be difficult to see on the macroscale, but bending a piece of metal or stretching into a thin wire requires major movement of atoms. And since bending the metal does not break it into pieces, the adjacent atoms must remain bonded together despite these large atomic movements. Apparently, the bonding electrons are not affected by this rearrangement of atoms. This is completely consistent with the idea we just discussed, that the electrons are free to move about many nuclei and are not just localized between two adjacent nuclei. When the atoms are rearranged by bending or stretching, the

electrons are free to immediately rearrange as well, and the bonding is preserved.

Our picture of a metal, based on these conclusions, is that the nuclei of the metal atoms are arranged in an array in the solid metal. The non-valence electrons in each metal, which are strongly attracted to each nucleus, remain localized near their own atoms. The valence electrons, though, are free to move about the positive centers of the nuclei and core electrons. Once you have this image in your head, you can see why chemists refer to this as the “electron sea model” of a metal. You should also be able to see how the properties of metals lead us to this electron sea image.

What about the shininess of metals? To understand this, we need to know what causes light to shine off of a surface. From our previous studies, we learned that light (electromagnetic energy) can be absorbed by atoms causing electrons to move from a lower energy state to a higher one. Similarly, light can be emitted from an atom with an electron moving from a higher energy state to a lower one. According to Einstein’s formula, the frequency of the light ν absorbed or emitted, when multiplied by a constant h , must match the energy difference ΔE between the two electron states: $\Delta E = h\nu$.

Because there are so many electrons in the electron sea which are involved in the bonding of the metal atoms together, there are many, many electron energy levels, a huge number in fact. So there are a correspondingly huge number of energy differences between these levels. This means that, when visible light hits the surface of a metal, the metal can easily absorb and reemit light of that frequency, reflecting the light and making the surface appear to shine.

Overall, we can see that the “electron sea” model of bonding of metal atoms together accounts for the properties of metals we have observed. It is worth thinking about how very different this model of bonding is from the covalent model of bonding in non-metals. We’ll come back to this contrast in the last section of this study.

Observation 2: Properties of Salts

There are many types of compounds formed by combining metals atoms and non-metal atoms. To simplify our discussion, we are going to focus on one specific type of compound called a salt. The common use of the term “salt” refers to one specific compound Sodium Chloride (NaCl), which is also a great example of the more general idea of a salt, so we’ll start with it and then consider some more examples.

What are the properties of NaCl ? They are quite different than the properties of the metals we just discussed. First, NaCl is a solid crystal and it is not at all malleable. A crystal of NaCl , say “rock salt,” cannot be molded into whatever shape we choose. Rather, it is very brittle. Hit it with a hammer and, unlike a piece of metal, it shatters into tinier fragments of the crystal. Similarly, it is not ductile. It cannot be rolled or stretched into a wire or a thread. Second, solid NaCl is not an electrical conductor. Instead it insulates against the movement of current even when an electric potential is applied. We can immediately conclude from these observations that the bonding model we developed for a metal is not going to work to describe bonding in NaCl . We’ll have to start from scratch.

There are other interesting properties of NaCl . One is that it dissolves easily in water, which most metals do not. And when dissolved in water, the resulting solution conducts electricity. Somehow then a current can pass through the salt solution, meaning that there are charged particles dissolved in the solution which carry the movement of charge. These charged particles turn out to be ions, Na^+ and Cl^- . Of course, this does not tell us whether there are ions in NaCl itself, since the interaction with the water molecules in the solution might change everything. Instead, we could try melting NaCl , so that we wind up with a liquid which is pure NaCl without any water. This takes a very high temperature, 808°C , indicating that there are strong forces at work in the solid NaCl crystal. When we melt NaCl , we find that the resulting liquid does in fact conduct electricity. Liquid NaCl thus consists of ions, Na^+ positive ions (“cations”) and Cl^- negative ions (“anions”).

As a result, we should expect that these same ions exist in the solid NaCl . How can we reconcile the existence of ions in solid NaCl with fact that it does not conduct an electric current? The answer is that a current is charge

in motion. Thus, the simple existence of an ion is not enough to carry a current. The ion must also be able to move, as electrons do in a metal, or as Na^+ and Cl^- do when dissolved in water. The ions in the solid cannot move, at least not very far, as we have seen from the fact that NaCl is not malleable. In fact, the Na^+ and Cl^- ions are basically fixed in place. From Coulomb's law, we know that opposite charges are strongly attracted to each other. We can conclude then that the bonding in NaCl is due to the attraction of Na^+ cations to Cl^- anions.

Why are there ions in the solid? The solid crystal itself is not electrically charged, so it isn't clear why each Na atom has lost an electron and each Cl atom has gained an electron. Let's look again at the properties of these very different kinds of atoms. We know that Na has low ionization energy, but it isn't zero. It still does require a lot of energy to ionize the valence electron. We know that Cl has a much higher ionization energy. More importantly, we also know that Cl has a high electron affinity, which means that a lot of energy is released when an electron is added to a Cl atom.

Is the energy released when the electron is attached to the Cl atom enough to ionize the Na atom? To find out, let's compare the ionization energy of Na to the electron affinity of Cl:

$\text{Na} \rightarrow \text{Na}^+ + \text{e}^-$ Ionization energy = 496 kJ/mol

$\text{Cl} + \text{e}^- \rightarrow \text{Cl}^-$ Electron affinity = -349 kJ/mol

Our answer is no. Taking an electron from a Na atom and giving it to a Cl atom costs a good amount of energy in total. This seems to suggest that the electron should not leave the Na atom and join the Cl atom, so NaCl shouldn't form ions and therefore shouldn't form a stable compound.

We haven't considered one key factor, however. The energy comparison above leads to the formation of independent positive and negative ions which don't interact with each other after the reaction is complete. But in reality, the Na^+ and Cl^- ions are very close to one another and attracted to one another. Coulomb's law tells us that this significantly lowers the energy. And there is even more to consider. A crystal of NaCl does not consist of a single Na^+ and a single Cl^- . Instead, it is an entire array of many positive

and negative ions. Each positive ion is surrounded by several negative ions. And each negative ion is surrounded by the same number of positive ions. (It turns out that number is 6.) Coulomb's law tells us that we get a huge lowering of energy from having all these opposite charges adjacent to one another. This energy is called the "lattice energy" and it is very large, -787 kJ/mol. This is much more than the energy deficit for ionizing both atoms, and accounts easily for the bonding in NaCl.

The bonding in NaCl is thus different than the covalent bonding in, say, HF or the metallic bonding in, say, Cu metal. For obvious reasons, we refer to this type of bonding as "ionic bonding."

Before concluding that ionic bonding is responsible for the stability of NaCl, we need to ask about the other primary property of NaCl mentioned above. Specifically, NaCl is brittle and not malleable. This is quite different from the property of a metal. In a metal, we could rearrange the atoms, for example by bending or by deforming with a hammer, and the atoms remain strongly bonded. But we cannot bend NaCl crystals, and if we hit them with a hammer, the bonding is destroyed as the crystal shatters. We simply cannot rearrange the atoms. It is clear that the bonding in NaCl depends very much on the arrangement of the atoms.

If we think about our ionic bonding model, this makes perfect sense. For the ionic bonding to work, the negative ions must remain surrounded by the positive ions and vice versa. Any attempt to rearrange these ions will result in positive ions adjacent to positive ions and negative ions next to negative ions. This will create strong repulsions, and the solid will fall apart. Ionic bonding thus accounts for the brittleness of NaCl.

So far, we've only looked at ionic bonding in NaCl as an example, but since we've seen that different covalent bonds have different energies, perhaps different ionic bonds have different energies. We compare different salts to see if there are different lattice energies in the ionic bonds. [\[link\]](#) shows a set of lattice energies for salts formed from alkali metals (Li, Na, K, Rb) and halogens (F, Cl, Br, I). There are some clear trends in these data. The largest lattice energy corresponds to the combination of the two smallest ions, Li^+ and F^- . The lattice energy decreases when either or both of the ions

are larger, with the smallest being for RbI, consisting of the two largest ions.

(kJ/mol)	F ⁻	Cl ⁻	Br ⁻	I ⁻
Li ⁺	1036	853	807	757
Na ⁺	923	787	747	704
K ⁺	821	715	682	649
Rb ⁺	785	689	660	630

Lattice Energies for Alkali Halides

Why would size be a determining factor in the lattice energy? We should recall that the lattice energy follows Coulomb's law. So, the closer the charges are to one another, the stronger is the interaction. Smaller ions can be closer together than larger ions. So the lattice energy is largest for the smallest ions.

Of course, Coulomb's law also involves the number of the charges. In all of the compounds in [\[link\]](#), the ions have a single +1 or -1 charge. We should look at compounds which contain doubly-charged ions. For common ions with +2 charges, we can look at the alkali earth metals. In [\[link\]](#), we can easily see that the lattice energies for salts of these ions are much larger than for the alkali metal ions. One final comparison would be a doubly-charged negative ion like O²⁻. Again, the lattice energies involving single positive charges with O²⁻ are larger, and the lattice energy is even larger still when both ions are doubly charged, as in MgO.

(kJ/mol)	F -	Cl -	Br -	I -	O 2-
Mg 2+	2936	2496	2397	2289	3923
Ca 2+	2608	2226	2131	2039	3517
Sr 2+	2475	2127	2039	1940	3312
Ba 2+	2330	2028	1948	1845	3120

Lattice Energies for Alkaline Earth Halides and Oxides (kJ/mol)

We can conclude that compounds of metals and non-metals are typically formed by ionic bonding, and the strength of this bonding can be clearly understood using Coulomb's law.

Observation 3: Properties and Bonding in Solid Carbon

In the first two observations of this study, we considered bonding in solids of two types, metals and salts. These are just two of the many types of solids, and not all solids are formed by either ionic bonding or metallic bonding. Far from it. We cannot look at every type of solid in this study, but it is worth considering one specific example which forms an interesting contrast to metals and salts. This example is diamond, one of several forms of pure solid carbon. (The other primary forms are graphene and the set of materials called fullerenes. We will postpone study of those materials for later.)

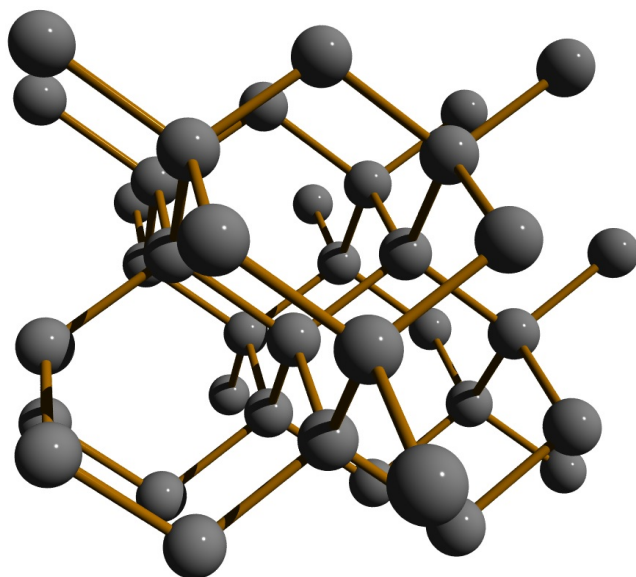
As always, we should begin with experimental observations to guide our understanding of diamond. What are its primary properties? It is a very hard solid, generally regarded as the hardest solid available in bulk. It is not malleable and would not be considered brittle like NaCl. It can be cleaved only with significant force. It has a very, very high melting point, over 3500 °C, and as an interesting note, it is the most thermally conducting material we know, meaning that it transfers heat better than any other substance. However, it does not conduct electricity.

What can we infer about the bonding in diamond from these properties? Since it is not brittle, we do not expect ionic bonding in diamond. This makes sense, since all of the atoms are carbon. But since it does not conduct electricity, we do not expect that the electrons are delocalized over the entire crystal, as they are in a metal. The bonding electrons must be more localized to individual nuclei. Since diamond is very hard and not malleable, the bonding must depend on the specific arrangement of the atoms, since, unlike a metal, it is very difficult to rearrange these atoms. Diamond won't bend!

So diamond has neither metallic bonding nor ionic bonding. But this is not a surprise, since we know already that carbon forms covalent bonds. We can recall that carbon atoms have a valence of 4 and have 4 valence electrons which they commonly share with other carbon atoms or with non-metal atoms to form covalent bonds. Since all of our observations suggest that the bonding electrons in diamond are localized, we can imagine that all of the bonding in diamond is covalent. That makes sense, based on our knowledge of the ways that carbon atoms bond with different elements.

Let's pick one carbon atom to start with. What if that carbon atom is bonded to four other carbon atoms, satisfying the octet rule for covalent bonding? And what if each of those four carbon atoms is, in turn, bonded to three additional carbon atoms. And those twelve carbon atoms are, again in turn, bonded to three additional carbon atoms. We can build an entire "network" of carbon atoms this way, as is illustrated in [\[link\]](#) where the C atoms are shown with bonds connecting them.

Carbon Atoms in the Diamond Network Lattice



Looking closely at this, it is clear that each carbon atom has a complete octet, satisfying its valence of 4. Thinking about this more carefully, it is also clear that this network does not have to end. We could continue building this network by adding more and more carbon atoms, each bonded to four other carbon atoms, building a huge molecule large enough to hold. Or to wear on a ring!

Does the bonding model in [\[link\]](#) account for the properties of diamond? The electrons are all localized, so we wouldn't expect diamond to conduct electricity. The atoms are very precisely arranged in the network and cannot be moved relative to one another without breaking some of the covalent bonds, so diamond is very hard and non-malleable. We call the bonding in diamond "network covalent", since the bonding is all covalent and creates a network of carbon atoms.

There is an important unanswered question: why do the carbon atoms sit in the particular geometry as they do in [\[link\]](#)? The answer is not obvious right now, and the question is the subject of the next concept study. For now, we'll simply note that a carbon atom with four single bonds will arrange those bonds in the shape of a tetrahedron. When all of the carbon atoms are networked together with this geometry, we get the network in [\[link\]](#).

A Model for Predicting the type of Bonding: Electronegativity

We have now seen three types of bonding in solids. In metallic bonding, the bonding valence electrons are delocalized in an “electron sea,” allowing current to flow and permitting distortions of the arrangements of the atoms. In ionic bonding, adjacent positive metal ions and negative non-metal ions are strongly attracted to each other in an array which places positive ions next to negative ions and vice versa. This creates a hard, brittle solid, not permitting rearrangement of the ions and not allowing electron flow in an electric current. In a solid covalent network like diamond, the bonding is the more familiar covalent sharing of an electron pair so that each non-metal atom in the network satisfies its valence in agreement with the octet rule. This makes a very hard solid which is neither brittle nor malleable, and this does not allow movement of electrons in a current.

It would be nice to add to our bonding model a way to understand or even to predict which of these types of bonding is expected for a particular solid. This would allow us to understand or predict the properties of the solid from the properties of the atoms which make it up. How shall we begin?

The most consistent trend we have seen is that bonding appears quite different for metals, non-metals, and combinations of metals and non-metals. At least from what we have observed so far, metal atoms bond to metal atoms with metallic bonding (hence the name!), metal atoms bond to non-metal atoms with ionic bonding, and non-metal atoms bond to non-metal atoms with covalent bonding. This suggests that we look at the differences between metal atoms and non-metal atoms. From our previous concept study, we know one major difference: the electronegativity of non-metals is quite high, whereas the electronegativity of metals is typically much lower.

Let's break this down in terms of the three types of bonding. The easiest case is ionic bonding. In this case, we have combined a metal with a non-metal, like Na with Cl, so we have combined atoms with high electronegativity with atoms with low electronegativity. Apparently, atoms with these properties tend to attract each other with ionic bonding. This makes sense: with very different electronegativities, the atoms are not likely

to share bonding electrons. It is likely that the very electronegative atoms will form negative ions and the weakly electronegative atoms will form positive ions, and the oppositely charged ions will attract each other. Thus, our model can be that, when a compound contains atoms with very different electronegativities, the compound is likely to be ionic bonded and have the properties of an ionic solid.

By process of elimination, the remaining types of bonding, metallic and covalent, must involve atoms with similar electronegativities. But something must distinguish these two in a way that we can predict. Metallic bonding is expected when all the atoms are metals and therefore have low electronegativity. Covalent bonding is expected when all the atoms are non-metals and therefore have relatively high electronegativity.

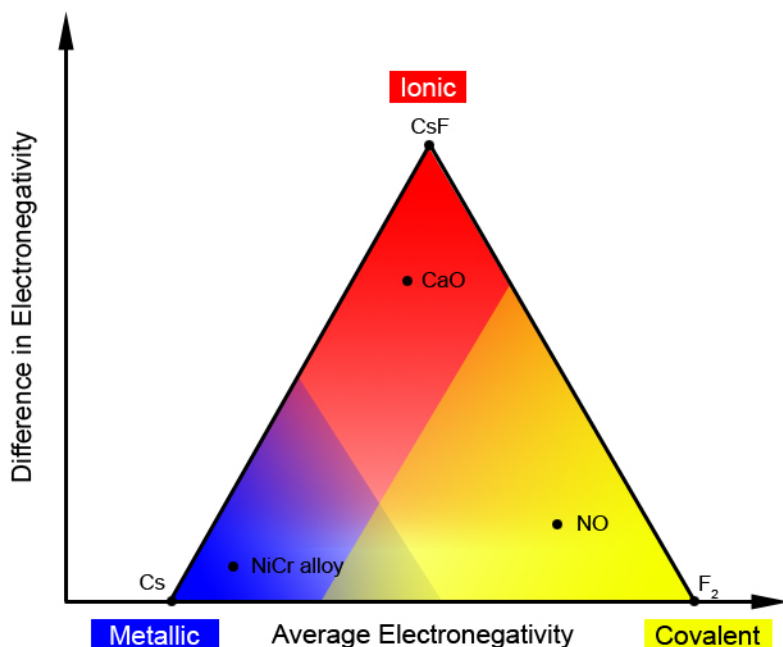
Here is the general summary for our model:

- When the bonded atoms in a compound all have low electronegativity, we should predict metallic bonding and the compound should be a solid with metallic properties.
- When the bonded atoms in a compound have very different electronegativities, we should predict ionic bonding and the compound should be a brittle, non-conducting solid.
- When the bonded atoms in a compound all have high electronegativity, we should predict covalent bonding.

In the last case, there are many types of solids possible, and the properties of a covalent compound depend very much on the types of solid which is formed. To illustrate, diamond and ammonia NH_3 are both covalent compounds, but the properties of these two compounds could hardly be more different. We'll need a more extensive model to predict what type of covalent compound will form.

This model leads to a simple picture for a reasonable prediction of the type of bonding. We need to consider both the differences in electronegativity between the atoms in a compound as well as the actual magnitudes of the electronegativities, either high or low. This means that, at least for binary compounds (those involving only 2 elements), we can create a chart showing both the magnitude of the electronegativities of the atoms (taken as

an average of the two electronegativities) and the difference between the two electronegativities. We wind up with a chart that looks like a triangle, as in [\[link\]](#). In fact, this is called a “bond type triangle.” A few compounds are shown on the triangle to illustrate how this model can be used successfully to predict the type of solid from the atoms involved.



Discussion Questions

1. Explain why the low ionization energy of a metal atom is important to the bonding in the metal.
2. The four metals Sc, Ti, V, and Cr have increasing nuclear charge in the order listed but have only small differences in ionization energy. On the basis of the electron configurations of these elements, explain this unexpected lack of variation.
3. It is often argued that alkali metals form ionic bonds with halogens (e.g. NaCl) because the Na atom can form an octet of electrons by

losing its valence electron, thus lowering its energy. Using experimental data, demonstrate that this is an incorrect model for explaining the formation of an ionic bond.

4. From the data in [\[link\]](#) and [\[link\]](#), identify three trends in the variation of lattice energies amongst these compounds, and explain these variations on the basis of Coulomb's law.
5. When a metal can be shaped into a spring, the metal can be stretched but will return to its original shape when released. Explain this behavior in terms of the bonding model of a metal. Suggest a reason why a salt cannot be used to make a spring.
6. Looking at the carbon atom network in diamond illustrated in [\[link\]](#), we could imagine that the bonding electrons are delocalized over the entire network, as in our electron sea model of a metal. Provide and explain experimental data which demonstrate that the electron sea model does not apply to solid carbon.
7. Why is it necessary to consider both electronegativity differences between bonded atoms and the average electronegativity of bonded atoms when analyzing the type of bond which is formed?
8. Why is the bond type diagram in [\[link\]](#) a triangle? That is, why is it not possible to observe compounds over the entire range of average electronegativity and electronegativity difference?

Molecular Geometry and Electron Domain Theory

Foundation

We begin by assuming a **Lewis structure model** for chemical bonding based on valence shell electron pair sharing and the octet rule. We thus assume the nuclear structure of the atom, and we further assume the existence of a valence shell of electrons in each atom which dominates the chemical behavior of that atom. A covalent chemical bond is formed when the two bonded atoms share a pair of valence shell electrons between them. In general, atoms of Groups IV through VII bond so as to complete an octet of valence shell electrons. A number of atoms, including C, N, O, P, and S, can form double or triple bonds as needed to complete an octet. We know that double bonds are generally stronger and have shorter lengths than single bonds, and triple bonds are stronger and shorter than double bonds.

Goals

We should expect that the properties of molecules, and correspondingly the substances which they comprise, should depend on the details of the structure and bonding in these molecules. The relationship between bonding, structure, and properties is comparatively simple in **diatomic** molecules, which contain two atoms only, e.g. HCl or O₂. A **polyatomic** molecule contains more than two atoms. An example of the complexities which arise with polyatomic molecules is molecular geometry: how are the atoms in the molecule arranged with respect to one another? In a diatomic molecule, only a single molecular geometry is possible since the two atoms must lie on a line. However, with a triatomic molecule (three atoms), there are two possible geometries: the atoms may lie on a line, producing a linear molecule, or not, producing a bent molecule. In molecules with more than three atoms, there are many more possible geometries. What geometries are actually observed? What determines which geometry will be observed in a particular molecule? We seek a model which allows us to understand the observed geometries of molecules and thus to predict these geometries.

Once we have developed an understanding of the relationship between molecular structure and chemical bonding, we can attempt an understanding

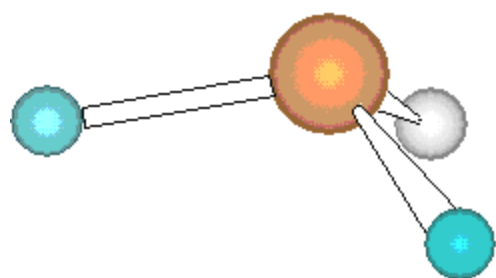
of the relationship of the structure and bonding in a polyatomic molecule to the physical and chemical properties we observe for those molecules.

Observation 1: Geometries of molecules

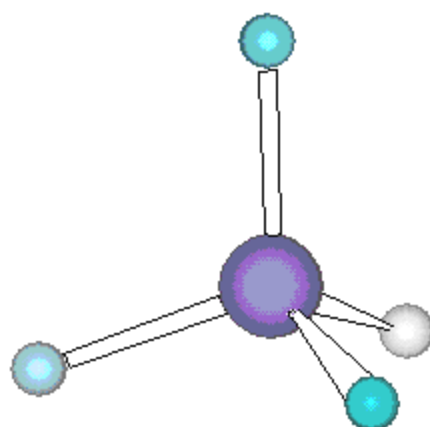
The geometry of a molecule includes a description of the arrangements of the atoms in the molecule. At a simple level, the molecular structure tells us which atoms are bonded to which. At a more detailed level, the geometry includes the lengths of all of these bonds, that is, the distances between the atoms which are bonded together, and the angles between pairs of bonds. For example, we find that in water, H_2O , the two hydrogens are bonded to the oxygen and each O-H bond length is 95.72 pm (where $1 \text{ pm} = 10^{-12} \text{ m}$). Furthermore, H_2O is a bent molecule, with the H-O-H angle equal to 104.5° . (The measurement of these geometric properties is difficult, involving the measurement of the frequencies at which the molecule rotates in the gas phase. In molecules in crystalline form, the geometry of the molecule is revealed by irradiating the crystal with x-rays and analyzing the patterns formed as the x-rays diffract off of the crystal.)

Not all triatomic molecules are bent, however. As a common example, CO_2 is a linear molecule. Larger polyatomics can have a variety of shapes, as illustrated in [\[link\]](#). Ammonia, NH_3 , is a pyramid-shaped molecule, with the hydrogens in an equilateral triangle, the nitrogen above the plane of this triangle, and a H-N-H angle equal to 107° . The geometry of CH_4 is that of a tetrahedron, with all H-C-H angles equal to 109.5° . (See also [\[link\]](#).) Ethane, C_2H_6 , has a geometry related to that of methane. The two carbons are bonded together, and each is bonded to three hydrogens. Each H-C-H angle is 109.5° and each H-C-C angle is 109.5° . By contrast, in ethene, C_2H_4 , each H-C-H bond angle is 116.6° and each H-C-C bond angle is 121.7° . All six atoms of ethene lie in the same plane. Thus, ethene and ethane have very different geometries, despite the similarities in their molecular formulae.

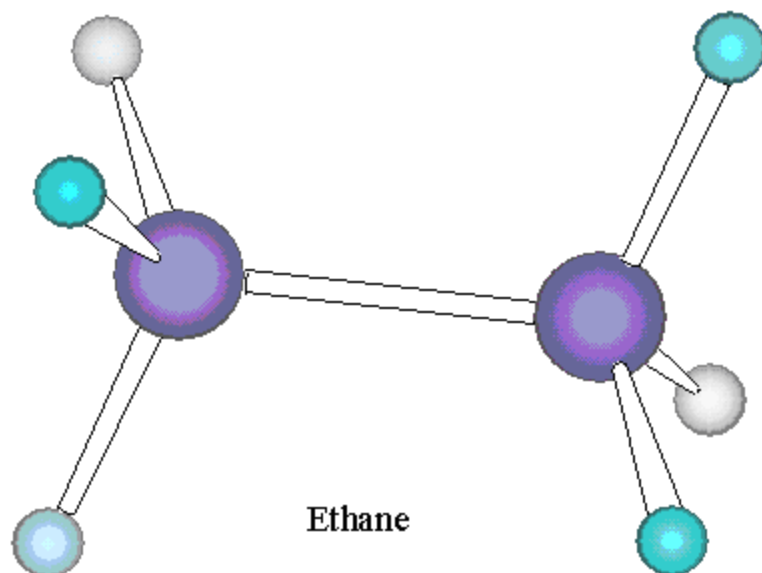
Molecular Structures



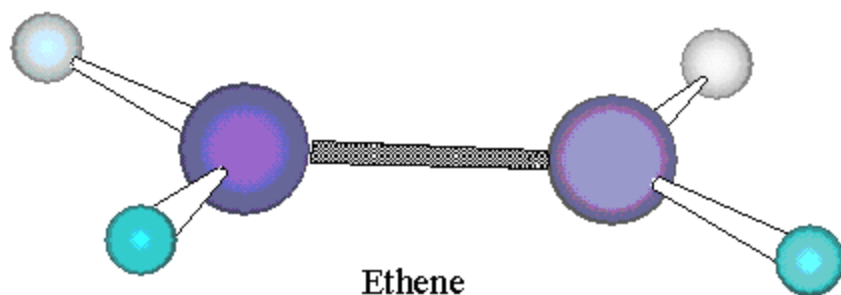
Ammonia



Methane



Ethane

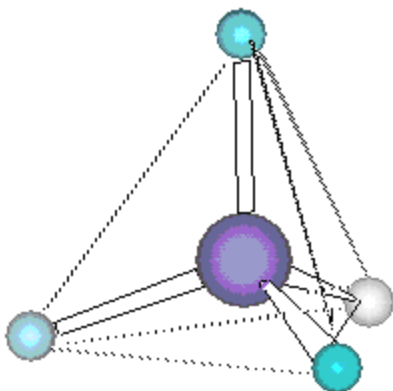


Ethene

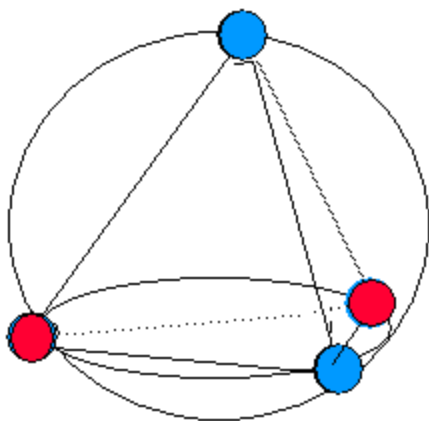
We begin our analysis of these geometries by noting that, in the molecules listed above which do **not** contain double or triple bonds (H_2O , NH_3 , CH_4 and C_2H_6), the bond angles are very similar, each equal to or very close to the tetrahedral angle 109.5° . To account for the observed angle, we begin with our valence shell electron pair sharing model, and we note that, in the Lewis structures of these molecules, the central atom in each bond angle of these molecules contains four pairs of valence shell electrons. For methane and ethane, these four electron pairs are all shared with adjacent bonded atoms, whereas in ammonia or water, one or two (respectively) of the electron pairs are not shared with any other atom. These unshared electron pairs are called **lone pairs**. Notice that, in the two molecules with no lone pairs, all bond angles are **exactly** equal to the tetrahedral angle, whereas the bond angles are only close in the molecules with lone pairs.

One way to understand this result is based on the mutual repulsion of the negative charges on the valence shell electrons. Although the two electrons in each bonding pair must remain relatively close together in order to form the bond, different pairs of electrons should arrange themselves in such a way that the distances between the pairs are as large as possible. Focusing for the moment on methane, the four pairs of electrons must be equivalent to one another, since the four C-H bonds are equivalent, so we can assume that the electron pairs are all the same distance from the central carbon atom. How can we position four electron pairs at a fixed distance from the central atom but as far apart from one another as possible? A little reflection reveals that this question is equivalent to asking how to place four points on the surface of a sphere spread out from each other as far apart as possible. A bit of experimentation reveals that these four points must sit at the corners of a tetrahedron, an equilateral triangular pyramid, as may be seen in [\[link\]](#). If the carbon atom is at the center of this tetrahedron and the four electron pairs are placed at the corners, then the hydrogen atoms also form a tetrahedron about the carbon. This is, as illustrated in [\[link\]](#), the correct geometry of a methane molecule. The angle formed by any two corners of a tetrahedron and the central atom is 109.5° , exactly in agreement with the observed angle in methane. This model also works well in predicting the bond angles in ethane.

Tetrahedral Structure of Methane



The dotted lines illustrate that the hydrogens form a tetrahedron about the carbon atom.



The same tetrahedron is formed by placing four points on a sphere as far apart from one another as possible.

We conclude that molecular geometry is determined by minimizing the mutual repulsion of the valence shell electron pairs. As such, this model of

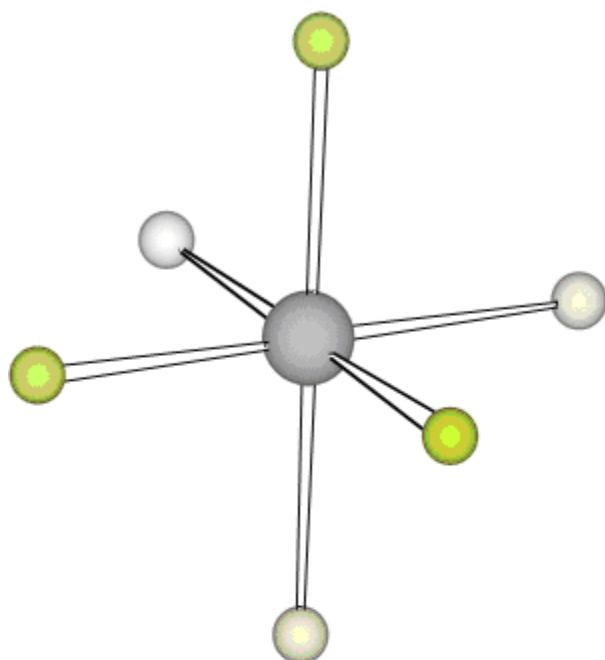
molecular geometry is often referred to as the **valence shell electron pair repulsion (VSEPR) theory** . For reasons that will become clear, extension of this model implies that a better name is the **Electron Domain (ED) Theory** .

This model also accounts, at least approximately, for the bond angles of H_2O and NH_3 . These molecules are clearly not tetrahedral, like CH_4 , since neither contains the requisite five atoms to form the tetrahedron. However, each molecule does contain a central atom surrounded by four pairs of valence shell electrons. We expect from our Electron Domain model that those four pairs should be arrayed in a tetrahedron, without regard to whether they are bonding or lone-pair electrons. Then attaching the hydrogens (two for oxygen, three for nitrogen) produces a prediction of bond angles of 109.5° , very close indeed to the observed angles of 104.5° in H_2O and 107° in NH_3 .

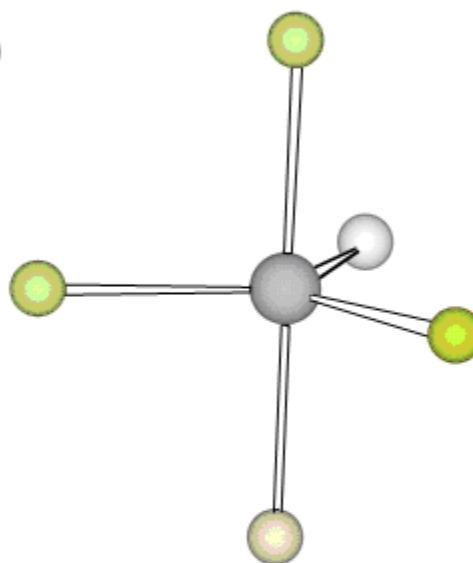
Note, however, that we do not describe the geometries of H_2O and NH_3 as "tetrahedral," since the **atoms** of the molecules do not form tetrahedrons, even if the valence shell electron pairs do. (It is worth noting that these angles are not exactly equal to 109.5° , as in methane. These deviations will be discussed [later](#).)

We have developed the Electron Domain model to this point only for geometries of molecules with four pairs of valence shell electrons. However, there are a great variety of molecules in which atoms from Period 3 and beyond can have more than an octet of valence electrons. We consider two such molecules illustrated in [\[link\]](#).

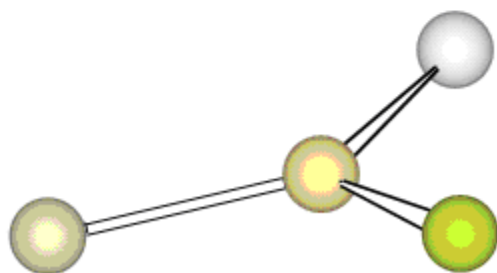
More Molecular Structures



Sulfur Hexafluoride



Phosphorous Pentachloride



Boron Trichloride

First, PCl_5 is a stable gaseous compound in which the five chlorine atoms are each bonded to the phosphorous atom. Experiments reveal that the geometry of PCl_5 is that of a **trigonal bipyramid**: three of the chlorine atoms form an equilateral triangle with the P atom in the center, and the other two chlorine atoms are on top of and below the P atom. Thus there must be 10 valence shell electrons around the phosphorous atom. Hence, phosphorous exhibits what is called an **expanded valence** in PCl_5 . Applying our Electron Domain model, we expect the five valence shell

electron pairs to spread out optimally to minimize their repulsions. The required geometry can again be found by trying to place five points on the surface of a sphere with maximum distances amongst these points. A little experimentation reveals that this can be achieved by placing the five points to form a trigonal bipyramid. Hence, Electron Domain theory accounts for the geometry of PCl_5 .

Second, SF_6 is a fairly unreactive gaseous compound in which all six fluorine atoms are bonded to the central sulfur atom. Again, it is clear that the octet rule is violated by the sulfur atom, which must therefore have an expanded valence. The observed geometry of SF_6 , as shown in [\[link\]](#), is highly symmetric: all bond lengths are identical and all bond angles are 90° . The F atoms form an **octahedron** about the central S atom: four of the F atoms form a square with the S atom at the center, and the other two F atoms are above and below the S atom. To apply our Electron Domain model to understand this geometry, we must place six points, representing the six electron pairs about the central S atom, on the surface of a sphere with maximum distances between the points. The requisite geometry is found, in fact, to be that of an octahedron, in agreement with the observed geometry.

As an example of a molecule with an atom with less than an octet of valence shell electrons, we consider boron trichloride, BCl_3 . The geometry of BCl_3 is also given in [\[link\]](#): it is **trigonal planar**, with all four atoms lying in the same plane, and all Cl-B-Cl bond angles equal to 120° . The three Cl atoms form an equilateral triangle. The Boron atom has only three pairs of valence shell electrons in BCl_3 . In applying Electron Domain theory to understand this geometry, we must place three points on the surface of a sphere with maximum distance between points. We find that the three points form an equilateral triangle in a plane with the center of the sphere, so Electron Domain is again in accord with the observed geometry.

We conclude from these predictions and observations that the Electron Domain model is a reasonably accurate way to understand molecular geometries, even in molecules which violate the octet rule.

Observation 2: Molecules with Double or Triple Bonds

In each of the molecules considered up to this point, the electron pairs are either in single bonds or in lone pairs. In current form, the Electron Domain model does **not** account for the observed geometry of C_2H_4 , in which each H-C-H bond angle is 116.6° and each H-C-C bond angle is 121.7° and all six atoms lie in the same plane. Each carbon atom in this molecule is surrounded by four pairs of electrons, all of which are involved in bonding, i.e. there are no lone pairs. However, the arrangement of these electron pairs, and thus the bonded atoms, about each carbon is not even approximately tetrahedral. Rather, the H-C-H and H-C-C bond angles are much closer to 120° , the angle which would be expected if **three** electron pairs were separated in the optimal arrangement, as just discussed for BCl_3 .

This observed geometry can be understood by re-examining the Lewis structure. Recall that, although there are four electron pairs about each carbon atom, two of these pairs form a double bond between the carbon atoms. It is tempting to assume that these four electron pairs are forced apart to form a tetrahedron as in previous molecules. However, if this were this case, the two pairs involved in the double bond would be separated by an angle of 109.5° which would make it impossible for both pairs to be localized between the carbon atoms. To preserve the double bond, we must assume that the two electron pairs in the double bond remain in the same vicinity. Given this assumption, separating the three **independent** groups of electron pairs about a carbon atom produces an expectation that all three pairs should lie in the same plane as the carbon atom, separated by 120° angles. This agrees very closely with the observed bond angles. We conclude that our model can be extended to understanding the geometries of molecules with double (or triple) bonds by treating the multiple bond as two electron pairs confined to a single **domain**. It is for this reason that we refer to the model as Electron Domain theory.

Applied in this form, Electron Domain theory can help us understand the linear geometry of CO_2 . Again, there are four electron pairs in the valence shell of the carbon atom, but these are grouped into only two domains of two electron pairs each, corresponding to the two $\text{C}=\text{O}$ double bonds. Minimizing the repulsion between these two domains forces the oxygen atoms to directly opposite sides of the carbon, producing a linear molecule. Similar reasoning using Electron Domain theory as applied to triple bonds

correctly predicts that acetylene, HCCH, is a linear molecule. If the electron pairs in the triple bond are treated as a single domain, then each carbon atom has only two domains each. Forcing these domains to opposite sides from one another accurately predicts 180° H-C-C bond angles.

Observation 3: Distortions from Expected Geometries

It is interesting to note that some molecular geometries (CH_4 , CO_2 , HCCH) are exactly predicted by the Electron Domain model, whereas in other molecules, the model predictions are only approximately correct. For examples, the observed angles in ammonia and water each differ slightly from the tetrahedral angle. Here again, there are four pairs of valence shell electrons about the central atoms. As such, it is reasonable to conclude that the bond angles are determined by the mutual repulsion of these electron pairs, and are thus expected to be 109.5° , which is close but not exact.

One clue as to a possible reason for the discrepancy is that the bond angles in ammonia and water are both **less** than 109.5° . Another is that both ammonia and water molecules have lone pair electrons, whereas there are no lone pairs in a methane molecule, for which the Electron Domain prediction is exact. Moreover, the bond angle in water, with two lone pairs, is less than the bond angles in ammonia, with a single lone pair. We can straightforwardly conclude from these observations that the lone pairs of electrons must produce a greater repulsive effect than do the bonded pairs. Thus, in ammonia, the three bonded pairs of electrons are forced together slightly compared to those in methane, due to the greater repulsive effect of the lone pair. Likewise, in water, the two bonded pairs of electrons are even further forced together by the two lone pairs of electrons.

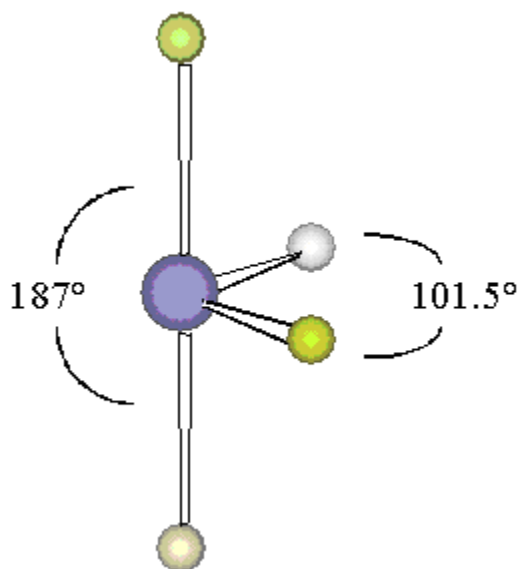
This model accounts for the comparative bond angles observed experimentally in these molecules. The valence shell electron pairs repel one another, establishing the geometry in which the energy of their interaction is minimized. Lone pair electrons apparently generate a greater repulsion, thus slightly reducing the angles between the bonded pairs of electrons. Although this model accounts for the observed geometries, why should lone pair electrons generate a greater repulsive effect? We must guess at a qualitative answer to this question, since we have no description

at this point for where the valence shell electron pairs actually are or what it means to share an electron pair. We can assume, however, that a pair of electrons shared by two atoms must be located somewhere between the two nuclei, otherwise our concept of "sharing" is quite meaningless. Therefore, the powerful tendency of the two electrons in the pair to repel one another must be significantly offset by the localization of these electrons between the two nuclei which share them. By contrast, a lone pair of electrons need not be so localized, since there is no second nucleus to draw them into the same vicinity. Thus more free to move about the central atom, these lone pair electrons must have a more significant repulsive effect on the other pairs of electrons.

These ideas can be extended by more closely examining the geometry of ethene, C_2H_4 . Recall that each H-C-H bond angle is 116.6° and each H-C-C bond angle is 121.7° , whereas the Electron Domain theory prediction is for bond angles exactly equal to 120° . We can understand why the H-C-H bond angle is slightly less than 120° by assuming that the two pairs of electrons in the C=C double bond produce a greater repulsive effect than do either of the single pairs of electrons in the C-H single bonds. The result of this greater repulsion is a slight "pinching" of the H-C-H bond angle to less than 120° .

The concept that lone pair electrons produce a greater repulsive effect than do bonded pairs can be used to understand other interesting molecular geometries. Sulfur tetrafluoride, SF_4 , is a particularly interesting example, shown in [\[link\]](#).

Molecular Structure of SF_4



Note that two of the fluorines form close to a straight line with the central sulfur atom, but the other two are approximately perpendicular to the first two and at an angle of 101.5° to each other. Viewed sideways, this structure looks something like a seesaw.

To account for this structure, we first prepare a Lewis structure. We find that each fluorine atom is singly bonded to the sulfur atom, and that there is a lone pair of electrons on the sulfur. Thus, with five electron pairs around the central atom, we expect the electrons to arrange themselves in a trigonal bipyramid, similar to the arrangement in PCl_5 in [\[link\]](#). In this case, however, the fluorine atoms and the lone pair could be arranged in two different ways with two different resultant molecular structures. The lone pair can either go on the axis of the trigonal bipyramid (i.e. “above” the sulfur) or on the equator of the bipyramid (i.e. “beside” the sulfur).

The actual molecular structure in [\[link\]](#) shows clearly that the lone pair goes on the equatorial position. This can be understood if we assume that the lone pair produces a greater repulsive effect than do the bonded pairs. With this assumption, we can deduce that the lone pair should be placed in the trigonal bipyramidal arrangement as far as possible from the bonded pairs. The equatorial position does a better job of this, since only two bonding pairs of electrons are at approximately 90° angles from the lone pair in this position. By contrast, a lone pair in the axial position is approximately 90° away from three bonding pairs. Therefore, our Electron Domain model

assumptions are consistent with the observed geometry of SF_4 . Note that these assumptions also correctly predict the observed distortions away from the 180° and 120° angles which would be predicted by a trigonal bipyramidal arrangement of the five electron pairs.

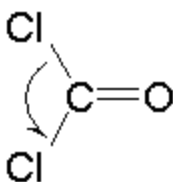
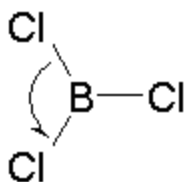
Review and Discussion Questions

1. Using a styrofoam or rubber ball, prove to yourself that a tetrahedral arrangement provides the maximum separation of four points on the surface of the ball. Repeat this argument to find the expected arrangements for two, three, five, and six points on the surface of the ball.
2. Explain why arranging points on the surface of a sphere can be considered equivalent to arranging electron pairs about a central atom.
3. The valence shell electron pairs about the central atom in each of the molecules H_2O , NH_3 , and CH_4 are arranged approximately in a tetrahedron. However, only CH_4 is considered a tetrahedral molecule. Explain why these statements are not inconsistent.
4. Explain how a comparison of the geometries of H_2O and CH_4 leads to a conclusion that lone pair electrons produce a greater repulsive effect than do bonded pairs of electrons. Give a physical reason why this might be expected.
5. Explain why the octet of electrons about each carbon atom in ethene, C_2H_4 , are not arranged even approximately in a tetrahedron.
6. Assess the accuracy of the following reasoning and conclusions:

A trigonal bipyramid forms when there are five electron domains. If one ED is a lone pair, then the lone pair takes an equatorial position and the molecule has a seesaw geometry. If two EDs are lone pairs, we have to decide among the following options: both axial, both equatorial, or one axial and one equatorial. By placing both lone pairs in the axial positions, the lone pairs are as far apart as possible, so the trigonal planar structure is favored.

7. Assess the accuracy of the following reasoning and conclusions:

The Cl-X-Cl bond angles in the [two molecules](#) are identical, because the bond angle is determined by the repulsion of the two Cl atoms, which is identical in the two molecules.



Measuring Energy Changes in Chemical Reactions

Introduction

Energy is a central theme of the study of Chemistry. The most common chemical reactions are carried out entirely for their production of energy. The most common sources of energy for use by humans are all chemical reactions. And the source of energy in the human body is entirely from chemical reactions. The industries of production, transportation, storage, and conversion of energy sources are overwhelmingly chemically based.

To this point in our studies, we have discussed energy extensively but only to help us understand the stability of atoms, the electronic structure of atoms, the stability of chemical bonds, the geometry of molecules, the bonding in metals and salts, and so forth. We have not yet studied the energy changes which accompany chemical reactions.

This study and the next mark a significant transition in our studies. Rather than focus entirely on the structure of atoms and molecules, we will now consider observations of chemical properties on the macroscopic level. One of the major goals of developing chemical models is to relate the structures of individual atoms and molecules to the properties we observe for substances and reactions in bulk amounts. This might seem an insurmountable task. Since a bulk sample of a substance may contain literally trillions of trillions of particles, relating the properties of those particles to the properties of the bulk seems to require an incomprehensible amount of information. In this study and those that follow, we begin that process. First, we make detailed observations about the amounts of energy which are released or absorbed during chemical reactions and develop a method for measuring reaction energies for bulk reactions. Then, in the next study, we will relate the energies of chemical bonds to the energies of chemical reactions. But first, we must relate the energies of chemical reactions to things we can measure directly and easily.

Introduction

To make any progress with energy in Chemistry, we must assume some basic principles about energy from Physics. Energy is the capacity to do work, where work is the application of a force over a distance. We can therefore tell whether an object possesses energy by determining whether it has the capacity to accelerate another object. Keep in mind that this is capacity to do work. It is not necessary for an object to actually do work to have energy. We often speak two broad types of energy, kinetic and potential. Kinetic energy is the energy associated with motion. An object in motion has the capacity to do work on another object by either pulling it, pushing it, or crashing into it, for examples. Potential energy is the energy associated with position. If by changing position an object can do work on another object, then it has potential energy. For example, a book on a table has potential energy because, if it were to fall to the floor, it could accelerate an object tied to it during the fall. During this study, we will relate chemical energy to these forms of energy.

One of the most important principles from Physics is the Conservation of Energy. This tells us that energy is neither created nor destroyed in any process, including a chemical process. Rather, energy is converted from one form to another during these processes. The energy conversion might possibly be from more useful forms to less useful forms of energy, but the energy is nevertheless conserved.

We will assume a foundation in the different types and energies of chemical bonds. In particular, we must recall that atoms are bonded together when their energy when bonded is lower than their energy when separated. Therefore, breaking a chemical bond requires the input of energy to do work on the bonded atoms by separating them. The more energy required, the stronger the bond.

Observation 1: Temperature Changes during Chemical Reactions

Since we are interested in the energy changes which happen during chemical reactions, it makes sense to look at reactions which have the most conspicuous energy changes, those which evolve heat. “Fire” is probably the first known human-controlled chemical reaction. Burning is now

understood as a combustion reaction of oxygen with a fuel, such as wood, oil, or natural gas. These reactions were all originally carried out primarily as sources of heat for warmth or cooking. In common terms, we use combustion of fuel to “heat up,” that is, to make something hotter or, better said, to raise the temperature of something.

It is pretty easy to observe that whatever is released during a chemical reaction which makes things hotter is a form of energy. For example, we can carry out the combustion reaction in a closed space that can expand, such as inside a cylinder with a piston inserted to close off the contents of the reaction. As the reaction occurs, we observe that the piston is pushed back, so work is done on the piston, meaning that the reaction has released energy to do that work. (This is the principal mechanism behind an internal combustion engine, of course.) When this transfer of energy creates temperature changes, we call this transfer “heat.”

Since heat can be defined in terms of temperature changes, this tells us that temperature and heat are very closely related concepts. We need a means to measure temperature. It is not enough for us to simply say that something hot has a high temperature. We need a measurement scale that allows us to compare “how hot” objects are compared to each other. There are lots of ways to do this. All of them are based on measuring some property which correlates to “hotness.” We most commonly use the expansion and contraction of liquid mercury in a glass tube, but we can observe expansion and contraction of solid metals, gases, etc. Or, we can observe other properties that vary with “hotness,” like the variation of resistance in wires or thermocouples or like the spectrum of infrared light emitted by a substance. This is why there are so many types of thermometers. As long as they are calibrated against each other so that they give the same reading when the temperature of a specific object is measured, all of them are useful.

Once we have a thermometer, we can easily show that heating an object causes its temperature to rise. Perhaps then temperature is the same thing as heat. Let’s test this idea and measure the temperature rise produced by a simple heat-producing chemical reaction like burning methane. As an example, we burn 1.0 g of methane gas and use the heat released to raise the

temperature of 1.000 kg of water (essentially 1.0 L of water). We observe that the water temperature rises by exactly 13.3 °C. This result is constant for this experiment. By performing this experiment repeatedly, we always find that the temperature of this quantity of water increases by 13.3 °C. Therefore, the same quantity of heat must always be produced by reaction of this quantity of methane. As such, it is very tempting to say that the amount of heat released by burning 1.0 g of methane is 13.3 °C. If this is true, then every time 1.0 g of methane is burned, a temperature rise of 13.3 °C should be observed.

However, if we burn 1.0 g of methane to heat 500 g of water instead, we observe a temperature rise of 26.6 °C. And if we burn 1.0 g of methane to heat 1.000 kg of iron, we observe a temperature rise of 123 °C. Therefore, the temperature rise observed depends on the quantity of material heated as well as what the substance is that is heated. Our temptation has led us astray. 13.3 °C is not an appropriate measure of this quantity of heat, since we cannot say that the burning of 1.0 g of methane "produces 13.3 °C of heat." Such a statement is clearly nonsense, so we must keep the concepts of temperature and heat distinct.

Observation 2: Heat and Heat Capacity, and Reaction Energy

Although temperature and heat are not the same concept, our data do tell us that they are related somehow. Let's look at some additional data. We know that if we burn 1.0 g of methane, the temperature rise in 1.0 kg of water is 13.3 °C or the temperature rise for 0.5 kg of water is 26.6 °C. What if we burn 2.0 g of methane? Experimentally, the temperature rise in 1.0 kg of water is 26.6 °C or the temperature rise for 0.5 kg of water is 53.2 °C. Look at those data carefully. We can reasonably assume that burning twice as much methane generates twice as much heat. And we see that it produces twice the temperature change of a fixed amount of water. This tells us that the temperature change for a fixed amount of water is proportional to the heat absorbed by the water.

Does this work for other materials? Earlier, we used the heat from burning 1.0 g of methane to heat 1.0 kg of iron, and we saw a temperature increase of 123 °C. If we burn 2.0 g of methane to heat 1.0 kg of iron, the

temperature increase is found to double to 246 °C. Again, the temperature change is proportional to the heat absorbed. Let's put this in symbols. If we call the quantity of heat q , and ΔT is the temperature rise produced by this heat, then we have observed that

Equation:

$$q = C \Delta T$$

where C is a proportionality constant. We need to be careful with this equation, though, because our data say that the relationship between q and ΔT depends on what material is heated (water or iron) and how much is heated (1.0 kg or 0.5 kg). So C depends on these same things: what material is heated and how much of the material is there. C is therefore a property of each material and is called the “heat capacity” of the material.

Our observations have already shown us that the temperature change is double for half as much water. We can repeat these observations for many different masses of water, and we also find that the temperature change is inversely proportional to the mass of the water. This means that the heat capacity C itself is proportional to the mass of the substance heated. (Look back at Equation 1 to convince yourself that this is true. For a fixed amount of heat, what happens to the temperature change and the heat capacity if we double the mass of water heated?) So now we rewrite Equation 1 with this new information:

Equation:

$$q = m C_s \Delta T$$

Here, m is the mass of the material being heated, and the proportional constant is now called the “heat capacity per gram” or more commonly the “specific heat.” Experiments show that, for any particular material, C_s is a relatively constant property of the material. (C_s actually varies slowly with the temperature, so it is about constant unless we make very large temperature changes.)

This equation so far is not very helpful, though, because we do not know values for the heat q or for the specific heat C_s . If we knew one, we would know the other from Equation 2, so somehow we have to devise an experiment to measure one or the other.

Here's one way to do the experiment. Since heat is a form of energy and energy is the capacity to do work, we just need to measure how much work can be done for a specific amount of heat, e.g. for burning a specific amount of methane. This is tricky, but we've already seen that we can use the heat generated by a reaction to push a piston back in a cylinder. If we burn 1.0 g of methane, we can measure how much work is done on the piston by measuring how much force is generated and for what distance. From these measurements and the rules of physics, we find that burning 1.0 g of methane can produce a maximum amount of work equal to 55.65 kJ.

(A second way to do the experiment is to use work to increase the temperature of water and to measure how much work is required to increase the temperature of water by 1 °C. We'll leave it as an exercise to devise a way to elevate temperature by doing work.)

What do the data tell us? If 55.65 kJ of work can be done by burning 1.0 g of methane, then burning 1.0 g of methane must produce 55.65 kJ of heat. This is q in Equation 2. But we have already measured that, for 1.0 kg of water, the temperature change is 13.3°C. This is ΔT in Equation 2, and m is 1000 g. From these data, we can directly calculate that, for water, $C_s = 4.184 \text{ J/g}\cdot^\circ\text{C}$. This is called the specific heat of water, or somewhat more loosely, the heat capacity of water. Pay attention to the units of this quantity, as they are unusual.

In similar ways, it is possible to find the specific heat or heat capacity of any material of interest. A set of specific heats for different substances is shown in [\[link\]](#). This is very valuable for predicting temperature changes in different materials. For our purposes, it has an even greater value. We can use this to determine the energy change in a chemical reaction.

Substance	C _p (J/g·°C)
Air (sea level)	1.0035
Ar (g)	0.5203
Au (s)	0.129
CH ₄ (g)	2.191
C ₂ H ₅ OH (l)	2.44
CO ₂ (g)	0.839
Cu (s)	0.385
Fe (s)	0.450
H ₂ (g)	14.30
H ₂ O (0 °C)	2.03
H ₂ O (25 °C)	4.184
H ₂ O (100 °C)	2.080
He (g)	5.19
Ne (g)	1.030
NaCl (s)	0.864
O ₂ (g)	0.918
Pb (s)	0.127

Specific Heat Capacities of Specific Substances at 25 °C (unless otherwise

noted)

Calorimetry: Measuring the Heat of a Chemical Reaction

Let's illustrate by analyzing the example of burning butane instead of methane. If we burn 1.0 g of butane and allow the heat evolved to warm 1.0 kg of water, we observe that an increase in the temperature of the water of 11.8 °C. Therefore, by [\[link\]](#), elevating the temperature of 1000 g of water by 11.8 °C must require 49,520 J = 49.52 kJ of heat. Therefore, burning 1.0 g of butane gas produces exactly 49.52 kJ of heat.

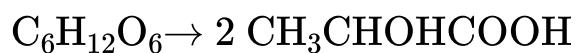
The method of measuring reaction energies by capturing the heat evolved in a water bath and measuring the temperature rise produced in that water bath is called calorimetry. Following this procedure, we can straightforwardly measure the heat released or absorbed in any easily performed chemical reaction.

By convention, when heat is absorbed during a reaction, we consider the quantity of heat to be a positive number: in chemical terms, $q > 0$ for an endothermic reaction. When heat is evolved, the reaction is exothermic and $q < 0$ by convention.

Observation 3: Hess' Law of Reaction Energies

The method of calorimetry we have developed works well provided that the reaction is easily carried out in a way that we can capture the energy transfer in a known quantity of water. But many reactions of great interest are very difficult to carry out under such controlled circumstances. Many biologically important chemical reactions may require the conditions and enzymes only available inside a cell. For example, conversion of glucose $C_6H_{12}O_6$ to lactic acid $CH_3CHOHCOOH$ is one of the primary means of providing energy to cells:

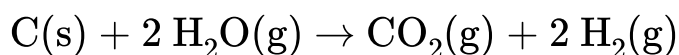
Equation:



Measuring the energy of this reaction is important to understanding the biological process of energy transfer in cells. However, we can't simply put glucose in a beaker and wait for it to turn into lactic acid. Very specific conditions and enzymes are required. We need to develop a different method for measuring the energy of this reaction, and this requires more experimentation.

To begin our observations, we will work with a few reactions for which we can measure the energy change. Hydrogen gas, which is of potential interest nationally as a clean fuel, can be generated by the reaction of carbon (coal) and water:

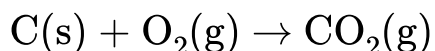
Equation:



Calorimetry reveals that this reaction requires the input of 90.1 kJ of heat for every mole of C(s) consumed.

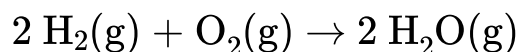
It is interesting to ask where this input energy goes when the reaction occurs. One way to answer this question is to consider the fact that Reaction (3) converts one fuel, C(s), into another, H₂(g). To compare the energy available in each fuel, we can measure the heat evolved in the combustion of each fuel with one mole of oxygen gas. We observe that

Equation:



produces 393.5 kJ for one mole of carbon burned; hence $q = -393.5 \text{ kJ}$. The reaction

Equation:



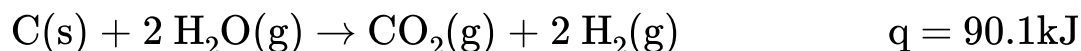
produces 483.6 kJ for two moles of hydrogen gas burned, so $q = -483.6 \text{ kJ}$. Therefore, more energy is available from the combustion of hydrogen fuel than from the combustion of carbon fuel. Because of this, we should not be

surprised that conversion of the carbon fuel to hydrogen fuel requires the input of energy.

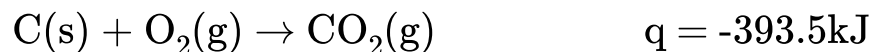
We can stare at the numbers for the heats of these reactions, 90.1 kJ, -393.5 kJ, -483.6 kJ, and notice a surprising fact. The first number 90.1 kJ, is exactly equal to the difference between the second number -393.5 kJ and the third number -483.6 kJ. In other words, the heat input in [\[link\]](#) is exactly equal to the difference between the heat evolved in the combustion of carbon ([\[link\]](#)) and the heat evolved in the combustion of hydrogen ([\[link\]](#)). This might seem like an odd coincidence, but the numbers from the data are too precisely equal for this to be a coincidence. Just as we do anytime we see a fascinating pattern in quantitative data, we should develop a model to understand this.

It is interesting that the energy of [\[link\]](#) is the difference between the energies in [\[link\]](#) and [\[link\]](#), and not the sum. One way to view this is to remember that the energy of a reaction running in reverse must be the negative of the energy of the same reaction running forward. In other words, if we convert reactants to products with some change in energy, and then convert the products back to the reactants, the change in energy of the reverse process must be the negative of the change in energy in the forward process. If this were not true, we could carry out the reaction many times and generate energy, which would violate the Law of Conservation of Energy.

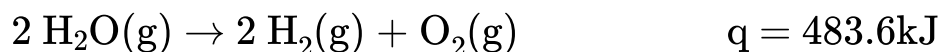
Let's list all three reactions together, but in doing so, let's reverse [\[link\]](#):
Equation:



Equation:

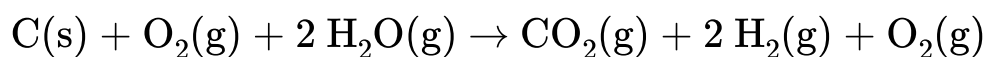


Equation:



What if we do both [\[link\]](#) and [\[link\]](#) at the same time?

Equation:



Since O₂ (g) is on both sides of this reaction, it is net neither a reactant nor product, so we could remove it without losing anything. [\[link\]](#) is then equivalent to [\[link\]](#), except that we carried it out by doing two separate reactions. What if we do [\[link\]](#) in two steps, first doing [\[link\]](#) and then doing [\[link\]](#)? That would be the same outcome as [\[link\]](#) so it must not matter whether we do [\[link\]](#) and [\[link\]](#) at the same time or one after the other. The reactants and products are the same either way.

What would be the energy of doing [\[link\]](#) and [\[link\]](#) either at the same time or in sequence? It must be the energy of [\[link\]](#) plus the energy of [\[link\]](#), of course. So if we add these together using the above numbers, the energy of doing both reactions together is $-393.5\text{kJ} + 483.6\text{kJ} = 90.1\text{kJ}$. This is the energy of [\[link\]](#) and it is experimentally exactly the same as the energy of [\[link\]](#).

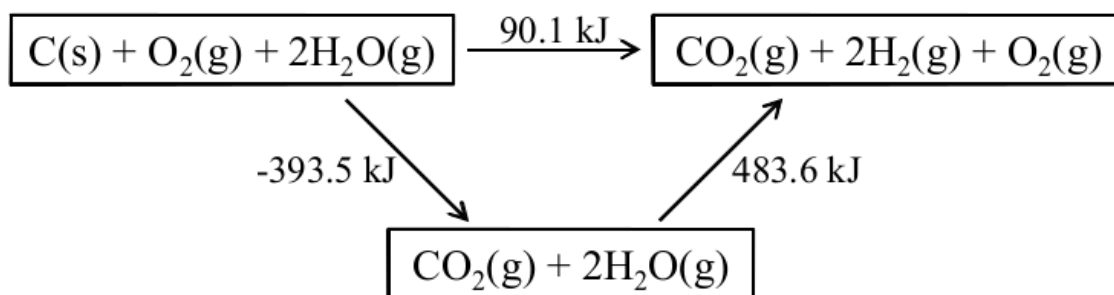
This is a new observation. We have found that the energy of a single reaction ([\[link\]](#)) is equal to the sum of the energies of two reactions ([\[link\]](#) and [\[link\]](#)), which together give the same total reaction as the single reaction. When the separate reactions add up to an overall reaction, the energies of the separate reactions add up to the energy of the overall reaction.

We could study many reactions in a similar manner to see if this pattern holds up. We find experimentally that it does. The pattern is therefore a new natural law called Hess' Law. Stated generally (but wordily), the energy of a reaction is equal to the sum of the energies of any set of reactions which, when carried out in total, lead from the same reactants to the same products. This is a powerful observation! (It is important to note here that we have omitted something from our observations. Hess' Law requires that all reactions considered proceed under similar conditions like temperature and pressure: we will consider all reactions to occur at constant pressure.)

Why would Hess' Law be true? Why doesn't it matter to the energy whether we carry out a reaction in a single step or in a great many steps which produce the same products? We might have guessed that more steps somehow require more energy or somehow waste more energy. But if so, our guess would be wrong. As such, it would be helpful to develop a model to account for this law to improve our intuition about reaction energies.

[\[link\]](#) gives us a way we can make progress based on the work we have already done. This is a just a picture of Hess' Law showing all of [\[link\]](#), [\[link\]](#), and [\[link\]](#). (Remember that the total reaction in [\[link\]](#) is exactly the same as the original reaction in [\[link\]](#).) In [\[link\]](#), the reactants $\text{C(s)} + 2 \text{H}_2\text{O(g)} + \text{O}_2\text{(g)}$ are placed together in a box, representing the reactant state of the matter before [\[link\]](#) occurs. The products $\text{CO}_2\text{(g)} + 2\text{H}_2\text{(g)} + \text{O}_2\text{(g)}$ are placed together in a second box representing the product state of the matter after [\[link\]](#). The reaction arrow connecting these boxes is labeled with the heat of [\[link\]](#) (which is also the heat of [\[link\]](#)), since that is the energy absorbed when the matter is transformed chemically from reactants to products in a single step.

Also in [\[link\]](#), we have added a box in which we place the same matter as in the reactant box but showing instead the products of carrying out [\[link\]](#). In other words, we will first do [\[link\]](#), producing $\text{CO}_2\text{(g)}$ but leaving the $\text{H}_2\text{O(g)}$ unchanged. Notice that the reaction arrow is labeled with the energy of [\[link\]](#). Now we can also add a reaction arrow to connect this box to the product box, because that reaction is just [\[link\]](#), producing $\text{H}_2\text{(g)}$ and $\text{O}_2\text{(g)}$ from the $\text{H}_2\text{O(g)}$. And we can label this reaction arrow with the energy of [\[link\]](#).



This picture of Hess' Law makes it clear that the energy of the reaction along the "path" directly connecting the reactant state to the product state is exactly equal to the total energy of the same reaction along the alternative "path" consisting of two steps which connect reactants to products. (This statement is again subject to our restriction that all reactions in the alternative path must occur under the same conditions, e.g. constant pressure conditions.)

Now let's take a slightly different view of [\[link\]](#). Visually make a loop by beginning at the reactant box and following a complete circuit through the other boxes leading back to the reactant box, summing the total energy of reaction as you go. If you go "backwards" against a reaction arrow, then reverse the sign of the energy, since a reverse reaction has the negative energy of the forward reaction. When we complete a loop and do the sum, we discover that the net energy transferred around the loop starting with reactants and ending with reactants is exactly zero. This makes a lot of sense when we remember the Law of Conservation of Energy: surely we cannot extract any energy from the reactants by a process which simply recreates the reactants. If this were not the case, in other words if the sum didn't equal zero, we could endlessly produce unlimited quantities of energy by following the circuit of reactions which continually reproduce the initial reactants. Experimentally, this never works since energy is conserved.

However, we do get a clearer understanding of why adding the reaction energies together gives the total energy of the overall reaction. Hess' Law is a consequence of the Law of Conservation of Energy.

Using Hess' Law to Measure Reaction Energy

It may be hard to remember now, but we started out with observations leading to Hess' Law because we wanted to find a way to measure the energy of a reaction which can't easily be found using calorimetry. Some reactions require special conditions which are hard to create in a laboratory where we can make measurements. We gave as an example fermentation of glucose to lactic acid:

Equation:



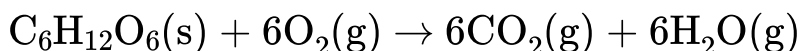
As we noted above, we can't simply put glucose in a beaker and wait for it to turn into lactic acid and measure a temperature change of a water bath. The reaction just doesn't happen without the assistance of enzymes in a cell.

So let's use Hess' Law, since we know that the energy of [\[link\]](#) will be the same as the sum of the energies of any set of reactions which adds up to [\[link\]](#). We just need to pick some reactions which are easy to carry out in the laboratory so that we can measure the energies of these reactions.

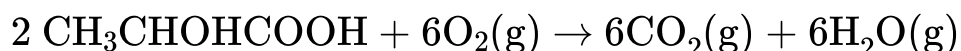
The easiest reactions to conduct, particularly with molecules containing carbon, hydrogen, and oxygen, are almost always combustion reactions. We can pretty easily burn these compounds, reacting them with oxygen to form $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{g})$. We can also pretty easily measure the energies of these combustion reactions using calorimetry, just like before.

Here is what the experiments give us:

Equation:



Equation:



We can now follow a two step process which is equivalent to converting one glucose molecule into two lactic acid molecules. First, we burn the glucose, and the energy evolved is -2808 kJ. Second, hypothetically, we convert the $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{g})$ into lactic acid and oxygen. Although we can't really do that hypothetical reaction, we don't need to. The energy of that second step is just the negative of the energy we measure for the combustion of two moles of lactic acid, which is -2668 kJ. Using Hess' Law, the overall energy for converting glucose to lactic acid then is just the measured energy of [\[link\]](#) plus the negative of the measured energy of

[\[link\]](#). This is equal to -140 kJ. We now have a means to measure the energy of a reaction which we can actually carry out!

This is a fairly general approach, applicable to most materials. By measuring the energies of combustion reactions and then summing those combustion reactions, we can calculate the energy of an overall reaction.

Review and Discussion Questions

1. How can the temperature of water be elevated by doing work on it? Devise a way to measure the amount work required to raise the temperature of a sample of water by 1°C .
2. Assume you have two samples of two different metals, X and Z. The samples are exactly the same mass.
 - (a) Both samples are heated to the same temperature. Then each sample is placed into separate glasses containing identical quantities of cold water, initially at identical temperatures below that of the metals. The final temperature of the water containing metal X is greater than the final temperature of the water containing metal Z. Which of the two metals has the larger heat capacity? Explain your conclusion.
 - (b) If each sample, initially at the same temperature, is heated with exactly 100 J of energy, which sample has the higher final temperature?
3. Using data from [\[link\]](#), provide two reasons with explanation why a hot object is much more efficiently cooled by placing it in water than leaving it in the open air, even when the air and the water are at the same temperature initially.
4. Explain how Hess' Law is a consequence of conservation of energy.
5. The enthalpy of formation of sucrose $\text{C}_6\text{H}_{12}\text{O}_6$ cannot be measured by the direct reaction of carbon, hydrogen and oxygen. Devise a method to measure ΔH_f for sucrose. What would you measure and how do these measured quantities relate to the ΔH_f for sucrose?

Reaction Energy and Bond Energy

Introduction

In the previous study, we developed detailed means to observe and measure the energy changes in chemical reactions. This ability is valuable all on its own, since managing the flow of energy from one form to another is a vital economic activity. But our work is not half done. In Chemistry, we seek not just to observe and measure, but also to model and to understand conceptually. We can make this point clearly by thinking about the following. Some chemical reactions produce energy, even in spectacular amounts. The detonation of a single gram of trinitrotoluene (TNT) produces about 4.2 kJ of energy. The reaction of a single gram of sodium metal (Na) with water produces about 8 kJ of energy. On the other hand, some reactions absorb energy, often evidenced by a significant cooling of the products or the surroundings of the reaction. For example, the hydration of ten grams of ammonium nitrate (NH_4NO_3) in an instant cold pack absorbs about 3.2 kJ of energy, causing it to be cold enough to treat minor athletic injuries.

How can we account for these great variations in the energies of reactions? Where does the energy come from in an exothermic reaction, and where does it in an endothermic reaction? Could we find a way to predict whether a reaction will be exothermic or endothermic? Answering these questions requires us to develop a model for energy transfer during chemical reactions.

Foundation

We will build significantly on the results of the previous concept study. We know how to measure energy changes in reactions. A reaction which releases energy into the environment is called an exothermic reaction, and the heat transfer $q < 0$. A reaction which absorbs energy from the environment is called an endothermic reaction, and the heat transfer $q > 0$.

Hess' Law, developed in the previous concept study, is an extremely important observation. Recall that Hess' Law tells us that the energy of a

reaction is equal to the sum of the energies of a set of reactions which add up to the overall reaction. Stated differently, the energy of a reaction does not depend on what “path” we follow in converting reactant to products, whether it be in a single reaction or a series of reactions. As long as we start with the same reactants and wind up with the same products, the energy of the reaction is the same.

Although this is not an observation or previous conclusion, we'll add to our foundation a definition of a new quantity, called “enthalpy.” To understand the usefulness of this new quantity, let's remember that, according to Hess' Law, if we start with a set of reactants and carry out a series of reactions which recreate the reactants, then the total energy change summed over that series of reactions has to be exactly zero. Using the Law of Conservation of Energy, this makes sense. We would not expect to be able to change the energy of a substance or substances without changing the state of those substances. In fact, for this reason, chemists call the energy of a substance a “state function,” meaning that the energy depends only on what state the substance is in (gas, liquid, solid; temperature; pressure).

An important fact about state functions is the change in a state function from start to finish during a process depends only on the value of the state function at the start and at the finish. The concept of a state function is somewhat analogous to the idea of elevation. The elevation of a city depends only on where the city is located. So, consider the difference in elevation between Houston and Denver. This difference is clearly independent of any path we choose to get from Houston to Denver. We could drive a direct route, we could take the train through Chicago, we could take a non-stop or a multi-stop flight, or we could depart Houston on a plane and parachute into Denver. Each path produces exactly the same elevation gain, equal to the elevation in Denver minus the elevation in Houston.

Since energy is a state function, the energy of the products depends only on the state of the products and the energy of the reactants only depends on the state of the reactants. So the energy change in going from reactants to products is just the energy of the products minus the energy of the reactants. We could choose any process that takes us from reactant to product. We do not even need to know what process or processes actually happen. You can

see how a state function like energy is reflected in our observation of Hess' Law.

Chemists choose to define a particular measure of the energy called the enthalpy, designated H . The enthalpy is a state function, just like the energy. The reason that chemists study the enthalpy is that the difference between the enthalpy of the products, and the enthalpy of the reactants, $H(\text{products}) - H(\text{reactants}) = \Delta H$, is equal to the heat transfer during a reaction carried out under constant pressure: $\Delta H = q$. Since a great many chemical processes, including essentially all biological processes, happen under constant pressure, this is a very helpful thing to know. For this reason, ΔH is often called the enthalpy of reaction or the heat of reaction. We will measure and calculate ΔH frequently in this concept study.

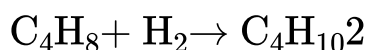
Observation 1: Enthalpy of Formation

Remember that our task is to understand what determines whether a reaction is exothermic or endothermic and why the energy transfer might be large or small. To do so, we need to get inside the reaction and find out what energy changes are taking place. And for this, Hess' Law and the state function H are extremely valuable. These allow us to choose any processes we want to carry out a chemical reaction, knowing that the energy transfer doesn't depend on what processes we pick. This frees us to pick processes to observe which are interesting or revealing to us. We want to pick processes which help us compare energies of reactants and products.

To do this, it is helpful to think of a standard to compare against. This is like defining elevation relative to sea level, making sea level the standard which is equal to zero elevation. We could have picked the zero to be the highest point on earth, the top of Mt. Everest, or the lowest point on earth, the bottom of the Marianas Trench, or the northernmost point, the North Pole, or anywhere else. We just need to pick something convenient which allows easy comparisons. Once we know every city's elevation relative to sea level, we can easily calculate the elevation change for every possible city to city trip without ever making any of those trips.

For the energy of chemical reactions, what standard shall we pick for comparing energies? One way is to pick the set of substances from which we can form all possible other materials. These are, of course, the elements. How would this work? Let's take a specific example. Butene, C_4H_8 , reacts with hydrogen to form butane, C_4H_{10} :

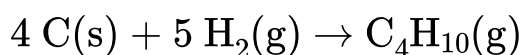
Equation:



To find the heat of this reaction ΔH , we need to compare the energy of the products to the energy of the reactants. We could do this by subtracting the energy of the products, relative to the energy of the elements, minus the energy of the reactants, again relative to the energy of the same elements. Clearly it would be very helpful to measure these energies.

The enthalpy of a substance, say butane, relative to the elements which make it up, carbon and hydrogen, is called the "enthalpy of formation" of the substance. This is the energy that is either absorbed or released when the substance is made from the elements in their standard form, and is labeled as ΔH_f . For example, for butane, the formation reaction from the elements is

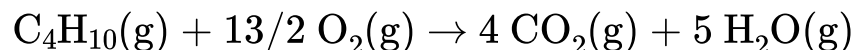
Equation:



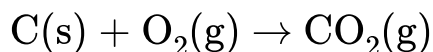
and the heat of this reaction is called the enthalpy of formation of butane. The enthalpy of formation tells us the energy of butane relative to the elements from which it could be formed.

Of course, for this to be useful, we have to measure this quantity. This formation reaction for butane, [\[link\]](#), is virtually impossible to perform in a controlled way so that we can measure the energy of the reaction. But, due to the work we did in the previous study on Hess' Law, we have a way to measure the energy of this reaction without actually carrying out the reaction. We can use an alternative pathway. Since carbon, hydrogen, and butane are all easy to burn, we can use combustion reactions as the alternative pathway and measure the energy of these reactions.

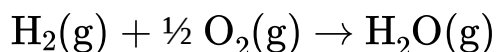
Equation:



Equation:



Equation:

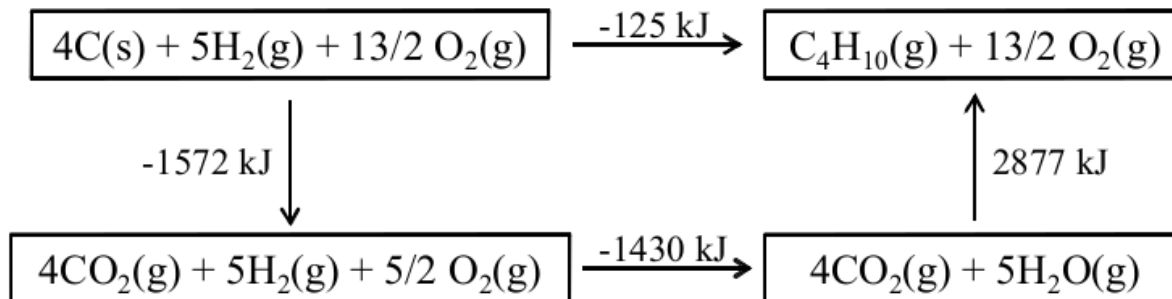


Using Hess' Law, we can use these three reactions and energies to find the energy of the formation reaction for butane, in other words, the enthalpy of formation of butane. [\[link\]](#) shows a diagram of Hess' Law for [\[link\]](#) from which we can write:

Equation:

$$\Delta H_f(\text{C}_4\text{H}_{10}) = \Delta H(\text{reaction 3}) - 4\Delta H(\text{reaction 4}) - 5\Delta H(\text{reaction 5})$$

This gives the enthalpy of formation of butane $\Delta H_f(\text{C}_4\text{H}_{10}) = -125 \text{ kJ/mol}$.



Remember that this enthalpy of formation of butane is the energy of [\[link\]](#) and therefore measures the energy of butane relative to the elements which make it up.

We can use this same approach to observe and measure the enthalpy of formation of any substance we are interested in. The enthalpies of formation of several interesting compounds are listed in [\[link\]](#). These values allow us to compare the energies of different compounds, since these are all relative to the same standard.

Substance	Formula	ΔH°_f (kJ/mol)
Acetylene	C_2H_2 (g)	226.7
Ammonia	NH_3 (g)	-46.1
Carbon Dioxide	CO_2 (g)	-393.5
Carbon Monoxide	CO (g)	-110.5
Ethanol	C_2H_5OH (l)	-277.7
Ethylene	C_2H_4 (g)	52.3
Glucose	$C_6H_{12}O_6$ (s)	-1260
Hydrogen Chloride	HCl (g)	-92.3
Iron(III) Oxide	Fe_2O_3 (s)	-824.2
Magnesium Carbonate	$MgCO_3$ (s)	-1095.8
Methane	CH_4 (g)	-74.8
Nitric Oxide	NO (g)	90.2

Water (g)	H ₂ O (g)	-241.8
Water (l)	H ₂ O (l)	-285.8

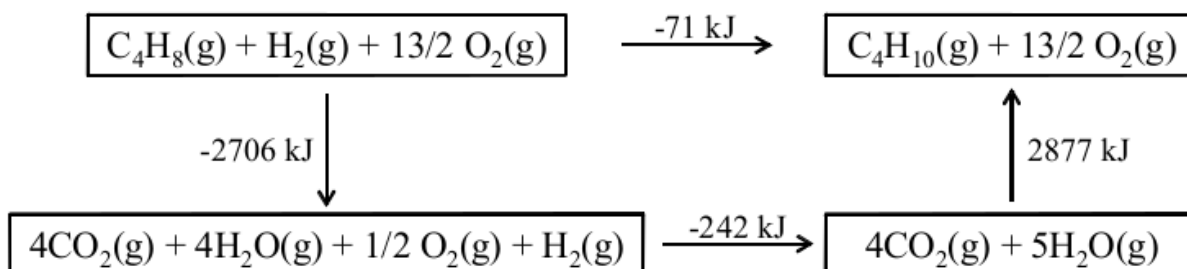
Standard Enthalpies of Formation for Various Substances at 25 °C

For example, thinking back to [\[link\]](#) where butene reacts to become butane, it is interesting to compare the enthalpy of formation of these two compounds to see that the energy of butene is higher than the energy of butane. In fact, we should be able to compare these numbers to measure the energy transfer in [\[link\]](#). Hess' Law once again comes in handy as is illustrated in [\[link\]](#). Now we can use an alternative pathway leading from reactants to products in two steps, first from reactants to the elements and then from the elements to the products. This means that we can write that the energy of [\[link\]](#) as

Equation:

$$\Delta H = \Delta H_f(\text{C}_4\text{H}_{10}) - \Delta H_f(\text{C}_4\text{H}_8)$$

What about the other reactant in [\[link\]](#), H₂? Why don't we include the enthalpy of H₂ in the calculation? [\[link\]](#) doesn't list an entry for the enthalpy of formation for H₂. This is because the formation reaction for H₂ would simply be H₂ → H₂, in other words, nothing needs to happen to form H₂ from elemental H₂ so there is no reaction and no enthalpy of formation for H₂.



Our approach for finding ΔH_{of} [\[link\]](#) is perfectly general. We can see that the heat of any reaction can be calculated from

Equation:

$$\Delta H^{\circ} = \Delta H_f^{\circ}(\text{products}) - \Delta H_f^{\circ}(\text{reactants})$$

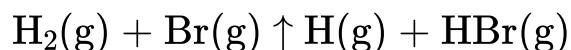
For this reason, extensive tables of ΔH_f° have been compiled and published. This allows us to calculate with complete confidence the heat of reaction for any reaction of interest, even including hypothetical reactions which may be difficult to perform or impossibly slow to react.

[\[link\]](#) is also a great way to interpret the energies of reactions. For example, if we observe an exothermic reaction, in other words if $\Delta H < 0$, we can say with confidence from [\[link\]](#) that $\Delta H_f(\text{reactants})$ is a larger number than $\Delta H_f(\text{products})$, that is, the reactants are higher in energy than the products.

Observation 2: Bond Energies in Chemical Reactions

Prior to this concept study and the previous one, we have discussed energy in the context of chemical bonding. We know that a chemical bond forms when the energy of the bonded atoms is lower than the energy of the separated atoms. The amount of energy required to break the bond and separate the atoms is called the bond energy. Since chemical reactions are all about breaking and making bonds, the energies of chemical reactions must be related to bond energies. Let's make some new observations which allow us to develop this relationship.

Let's observe two simple examples. First, the reaction

Equation:

is observed to be endothermic with a heat of reaction of 70 kJ/mol. What happens in this reaction seems pretty simple. The reaction could be viewed as consisting entirely of the breaking of the H_2 bond followed by the formation of the HBr bond. Using Hess' Law and following the process which first breaks the H_2 bond and then forms the HBr bond, we must input energy equal to the bond energy of H_2 (436 kJ/mol), and in forming the HBr

bond we recover output energy equal to the bond energy of HBr (366 kJ/mol). The enthalpy of [\[link\]](#) must be equal to difference in these bond energies, 70 kJ/mol.

Note that it does not matter whether the reaction actually occurs by first breaking a bond and then forming a new one. In fact, it probably does not happen this way. The two actions, bond breaking and bond formation, actually happen simultaneously as the H atom moves smoothly from the other H atom to the Br atom. But, by Hess' Law, we can follow the pathway which first breaks the bond and then forms the new bond and still get the energy of the reaction correct.

This alternative pathway involving breaking and making bonds is very revealing. Now we can answer the question for this reaction of where the energy "goes" during the endothermic reaction. The reason this reaction absorbs energy is that the bond which must be broken, H₂, is stronger than the bond which is formed, HBr. Note that energy is released when the HBr bond is formed, but the amount of energy released is less than the amount of energy required to break the H₂ bond in the first place. The molecule with the weaker bond, HBr, is higher in energy than the molecule with the stronger bond, H₂.

A second example is similar:

Equation:



This reaction is exothermic with $\Delta H^\circ = -103 \text{ kJ/mol}$. In this case, we must break an H₂ bond, with energy 436 kJ/mol, and a Br₂ bond, with energy 193 kJ/mol. Since two HBr molecules are formed, we must form two HBr bonds, each with a bond energy of 366 kJ/mol. In total, then, breaking the bonds in the reactants requires 629 kJ/mol, and forming the new bonds releases 732 kJ/mol, for a net release of -103 kJ/mol. This calculation reveals that we have to compare not just the strengths of the bonds broken and formed but also the number of bonds broken and formed. In this case, even though the HBr bond is weaker than the H₂ bond, there are two HBr

bonds formed and this releases more energy, making the reaction exothermic.

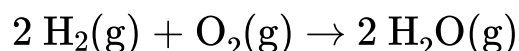
Observation 3: Bond Energies in Polyatomic Molecules

So far in this study, we have discussed the energies of substances in two different ways. One is to compare the energy of the substance to the energies of the elements which make it up, what we have called the enthalpy of formation. The other is to compare the energy of the substance to the separated atoms which make it up, what we have called the bond energy. These two would seem to be closely related. Since it would be helpful to understand that relationship, we need to look at data which connect the two.

We have actually already considered one reaction where the connection should be relatively easy. [\[link\]](#) above involves the formation of HBr from elemental H₂ and Br₂. Since two HBr molecules are formed, the energy of [\[link\]](#) is just double the enthalpy of formation of HBr. We have also calculated the energy of [\[link\]](#) from the bond energies of HBr, H₂ and Br₂. In this case, it is clear that the formation energy of HBr is easy to understand in terms of the relative strengths of the bonds of the reactants and products.

It seems that this should be generally true. Let's look at some additional data, this time involving a reaction with molecules which contain more than two atoms. A simple example is the combustion of hydrogen gas discussed previously:

Equation:



This is an explosive reaction, producing 483.6 kJ per mole of oxygen. Note that this is also the formation reaction for H₂O(g). Calculating the enthalpy of formation of H₂O(g) from bond energies requires us to know the bond energies in H₂O. In this case, we must break not one but two bonds:

Equation:



The energy required to perform this reaction is measured to be 926.9 kJ/mol. Therefore, the energy of [\[link\]](#) must be the energy required to break two H₂ bonds and one O₂ bond minus twice the energy of [\[link\]](#). We calculate that $\Delta H^\circ = 2(436 \text{ kJ/mol}) + (498.3 \text{ kJ/mol}) - 2(926.9 \text{ kJ/mol}) = -483.5 \text{ kJ/mol}$, which agrees with the measured enthalpy of formation. What we learn from this calculation is that the combustion of hydrogen gas in [\[link\]](#) is strongly exothermic because of the very large amount of energy released when two hydrogen atoms and one oxygen atom form a water molecule.

Let's look a little more closely at [\[link\]](#). It is tempting to use the energy of [\[link\]](#) to calculate the energy of an O-H bond, since we break two O-H bonds in the reaction and breaking the two O-H bonds in water requires 926.9 kJ/mol. It must be true that both O-H bonds are identical, so it seems that breaking a single O-H bond requires $(926.9 \text{ kJ/mol})/2 = 463.5 \text{ kJ/mol}$.

We can check this by looking at the energy of the reaction

Equation:



in which only one O-H bond is broken. Data tell us that the energy of this reaction is 492 kJ/mol. This is quite a bit higher than what we just predicted. Where did we go wrong with our prediction?

If we compare [\[link\]](#) and [\[link\]](#) and use Hess' Law, we can calculate the energy of breaking the bond in an OH(g) molecule:

Equation:



Equation:



Equation:

Therefore, the energy required to break an O-H bond in H₂O is quite a bit different than the energy required to break the O-H bond in the OH diatomic molecule. Stated differently, it requires more energy to break the first O-H bond in water than is required to break the second O-H bond. Does this mean that the two bonds in H₂O are not the same? Of course, the two bonds in H₂O are identical so they have the same bond strength. However, after the first O-H bond is broken, the O-H bond which remains no longer has the same bond strength. Once the first H atom has departed, along with its electron, the bonding of the atoms left behind has changed. It's pretty clear that the remaining O-H bond is weakened when the first O-H bond is broken.

Our observation that different O-H bonds have different bond energies is general when we look at more data. For example, we find that the energy required to break the O-H bond in methanol (CH₃OH) is 437 kJ/mol, which differs substantially from the energy of [\[link\]](#) and differs somewhat from the energy in [\[link\]](#).

This makes sense, but it does greatly complicate our measurements and calculations. To be able to use bond energies to calculate reaction energies, we would need to know the energy of each successive bond breaking in a molecule with more than one bond. This would be an overwhelming amount of data to collect and store. Rather than become discouraged, we need to develop a model and this requires more observations.

Let's consider C-H bonds. The energy required to break a single C-H bond in methane (CH₄) is 435 kJ/mol, but the energy required to break all four C-H bonds in methane is 1663 kJ/mol, which is not equal to four times the energy of one bond. This means that breaking each C-H bond in succession gives different energies each time. As another such comparison, the energy required to break a C-H bond is 400 kJ/mol in trichloromethane (HCCl₃), 414 kJ/mol in dichloromethane (H₂CCl₂), and 422 kJ/mol in chloromethane (H₃CCl).

These observations reinforce our observation that there is no single energy associated with a single type of bond, e.g. a C-H bond. On the other hand, we can see that the bond energies for similar bonds in similar molecules are close to one another. The C-H bond energies in the three chloromethanes above illustrate this quite well. The average C-H bond energy in the three chloromethanes molecules is 412 kJ/mol, which is close to each of the individual bond energies. Likewise, the average of the C-H bond energies in methane is $(1663 \text{ kJ/mol})/4 = 416 \text{ kJ/mol}$, which is also close to the value above and is not that far from the value for breaking the first C-H bond.

If we observe the bond energy for a specific type of bond (e.g. a C-H bond) in many molecules, we generally find that we can approximate the bond energy in any specific molecule by an average of the energies of similar bonds over many molecules. This means that it is valuable to have a table of the average energy of each type of bond, since these will be close to the value of the energy of that bond in any given molecule. These data are shown in [\[link\]](#).

Bond	Bond Energy (kJ/mol)	Bond	Bond Energy (kJ/mol)	Bond	Bond Energy (kJ/mol)
H-I	297	I-I	151	C-O	360
H-P	322	F-F	159	C=O	743
H-Br	364	Br-Br	193	C-Cl	339
H-S	368	Cl-Cl	243	O-O	142
H-N	389	C-C	347	O=O	496

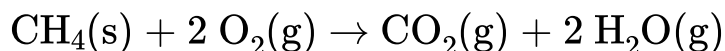
H-C	412	C=C	611	N-N	163
H-Cl	431	C≡C	837	N=N	418
H-H	436	C-N	305	N≡N	946
H-O	463	C=N	615	N-O	222
H-F	565	C≡N	891	N=O	590

Average Bond Energies

These average bond energies are very informative because they can be used to estimate the heat of a reaction without measuring all of the required bond energies.

Consider for example the combustion of methane to form water and carbon dioxide:

Equation:



We can estimate the heat of this reaction by using average bond energies. We must break four C-H bonds at an energy cost of approximately 4×412 kJ/mol and two O₂ bonds at an energy cost of approximately 2×496 kJ/mol. Forming the bonds in the products releases approximately 2×743 kJ/mol for the two C=O double bonds and 4×463 kJ/mol for the O-H bonds. Net, the heat of reaction is thus approximately $\Delta H^\circ = 1648 + 992 - 1486 - 1852 = -698$ kJ/mol. This is only a rough approximation to the actual heat of combustion of methane, -890 kJ/mol. Therefore, we cannot use average bond energies to predict accurately the heat of a reaction. But we can get an estimate, and this may be sufficiently useful. Moreover, we can use these calculations to gain insight into the energetics of the reaction. For example, [link](#) is strongly exothermic, which is why methane gas (the primary component in natural gas) is an excellent fuel. From our calculation, we can see that the reaction involved breaking six bonds and forming six new bonds. The bonds formed, particularly the C=O bonds, are

substantially stronger than the bonds broken, and this accounts for the net release of significant energy during the reaction.

Review and Discussion Questions

1. Consider the reaction



Draw Lewis structures for each of N_2O_4 and NO_2 . On the basis of these structures, predict whether the reaction is endothermic or exothermic, and explain your reasoning.

2. Why is the bond energy of H_2 not equal to ΔH_f° of H_2 ? For what species is the enthalpy of formation related to the bond energy of H_2 ?
3. Suggest a reason why ΔH° for the reaction



is not equal to ΔH° for the reaction



4. Determine whether the reaction is exothermic or endothermic for each of the following circumstances:
 1. The combustion of the products is more exothermic than the combustion of the reactants.
 2. The enthalpy of formation of the products is greater than the enthalpy of formation of the reactants.
 3. The total of the bond energies of the products is greater than the total of the bond energies for the reactants.

Physical Properties of Gases

Introduction

The individual molecules of different compounds have characteristic properties, such as mass, structure, geometry, bond energies, bond lengths, bond angles, polarity, diamagnetism, or paramagnetism. We have not yet considered the properties of mass quantities of matter, such as density, phase (solid, liquid or gas) at room temperature, boiling and melting points, reactivity, and so forth. These are properties which are not exhibited by individual molecules. It makes no sense to ask what the boiling point of one molecule is, nor does an individual molecule exist as a gas, solid, or liquid. However, we do expect that these material or bulk properties are related to the properties of the individual molecules. Our ultimate goal is to relate the properties of the atoms and molecules to the properties of the materials which they comprise. This is where our work on the properties of individual atoms and molecules begins to pay big dividends in our understanding of matter.

This goal is, in general, very difficult to achieve both conceptually and quantitatively, and for many substances, relating the molecular properties to bulk properties is an active area of research. But there are many substances and properties for which we can make conceptual progress, and in some cases, we can even develop quantitative relationships. In the next Concept Development Study, we will study the relationship between the properties of gases and the properties of the individual particles which make up gases. In this Concept Development Study, we lay the groundwork for that study by analyzing the physical properties of gases, including pressure, density, and temperature.

Foundation

We assume as our starting point the Atomic Molecular Theory, which states that all matter is composed of discrete particles. The elements consist of identical atoms, and compounds consist of identical molecules, which are particles containing small whole number ratios of atoms. We also assume

that we have determined a complete set of relative atomic weights, allowing us to determine the molecular formula for any compound.

Of particular use will be Avogadro's Law, which states that equal volumes of gases contain equal numbers of gas particles, regardless of the type of gas particles, provided that the volumes are taken at equal pressure and temperature. You may recall that Avogadro based this statement on the Law of Combining Volumes.

Observation 1: Pressure-Volume Measurements on Gases

It is an everyday observation that air has a "spring" to it: if you squeeze a balloon, the balloon rebounds to its original shape. As you pump air into a bicycle tire, the air pushes back against the piston of the pump.

Furthermore, this resistance of the air against the piston clearly increases as the piston is pushed farther in. The "spring" of the air is measured as a pressure, where the pressure P is defined:

$$P = F/A$$

F is the force exerted by the air on the surface of the piston head, and A is the surface area of the piston head.

Pressure is measured in a variety of ways using a variety of units. One simple unit is the "atmosphere" (atm), where 1 atm is approximately the pressure exerted by the gases in the atmosphere at sea level. Another unit is "torr," which is equal to 1/760 of 1atm. The torr was defined by the height of a column of mercury in millimeters. Since 1 atm pressure can support a column of mercury 760 mm high, then 1 torr supports a column of mercury 1 mm high. Consequently, pressure is often measured in "mm Hg." The standard unit of pressure is the "Pascal" (Pa), technically defined as 1 Newton per square meter. For our purposes, we only need to know that $1 \text{ atm} = 760 \text{ torr} = 101,325 \text{ Pa}$.

To observe the pressure-volume relationship for gases, we trap a small quantity of air in a syringe (a piston inside a cylinder) connected to a

pressure gauge, and we measure both the volume of air trapped inside the syringe and the pressure reading on the gauge.

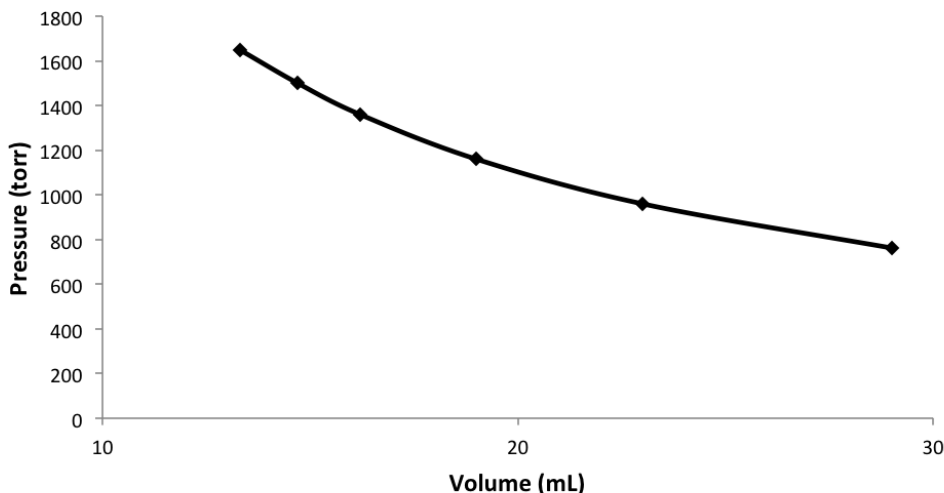


In one such sample measurement, we might find that the volume of gas trapped inside the syringe is 29.0 mL at atmospheric pressure (760 torr). If we then compress the syringe slightly, the volume becomes smaller, now 23.0 mL. We feel the increased spring of the air resisting this compression, and this is registered on the gauge as an increase in pressure to 960 torr. It is simple to make many measurements in this manner. A sample set of data appears in Table 1. We note that, in agreement with our experience with gases, the pressure increases as the volume decreases. These data are plotted in Figure 1, and the graph shows that as volume increases, pressure decreases. Notice also that the graph is not a straight line. A change of 6 mL of volume produces a 200 torr change in the pressure from 760 torr to 960 torr. However, a change of only 4 mL of volume is needed to produce another 200 torr change in the pressure from 960 torr to 1160 torr. Equal changes in pressure do not arise from equal changes in volume, and equal changes in volume do not produce equal changes in pressure.

Volume (mL)	Pressure (torr)
29	760
23	960
19	1160
16.2	1360
14.7	1500
13.3	1650

Sample Data from Pressure-Volume Measurement

Figure 1



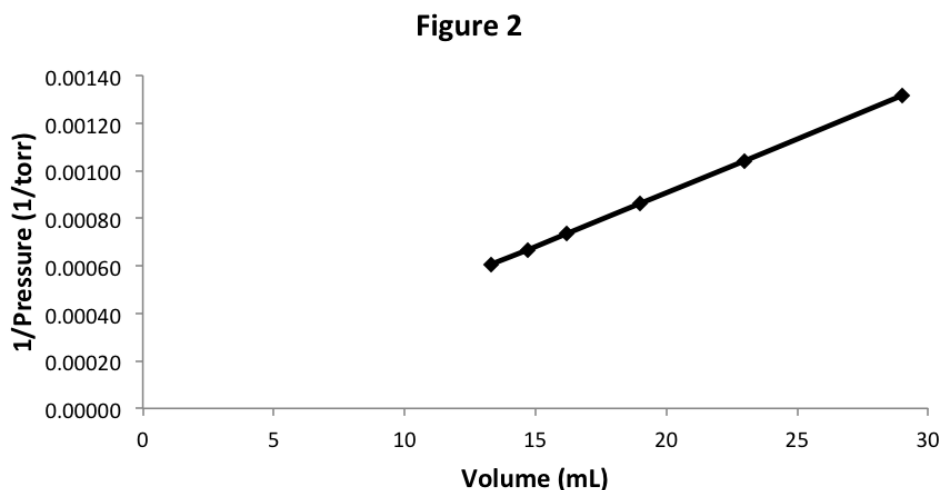
Since the relationship between pressure changes and volume changes does not appear to be simple, we should ask whether there is a quantitative relationship between the pressure and volume measurements. One way that we can try to explore this possibility is to try to plot the data in such a way that the quantity on the x-axis increases so does the quantity on the y-axis. Since pressure decreases when the volume increases, the inverse of the pressure ($1/P$) will increase when the volume increases. In Table 2 and Figure 2, we calculate and plot $1/P$ for each of the volumes in Table 1.

Volume (mL)	Pressure (torr)	1/Pressure(1/torr)
29	760	0.00132
23	960	0.00104
19	1160	0.00086
16.2	1360	0.00074

Volume (mL)	Pressure (torr)	1/Pressure(1/torr)
14.7	1500	0.00067
13.3	1650	0.00061

Analysis of Sample Data from Table 1

Notice also that, with elegant simplicity, the data points form a straight line. Furthermore, the straight line seems to connect to the origin (0,0). If we were to write the equation for this straight line with its y-intercept as zero and its slope as k, the equation relating pressure and volume is:



$$1/P = k \times V$$

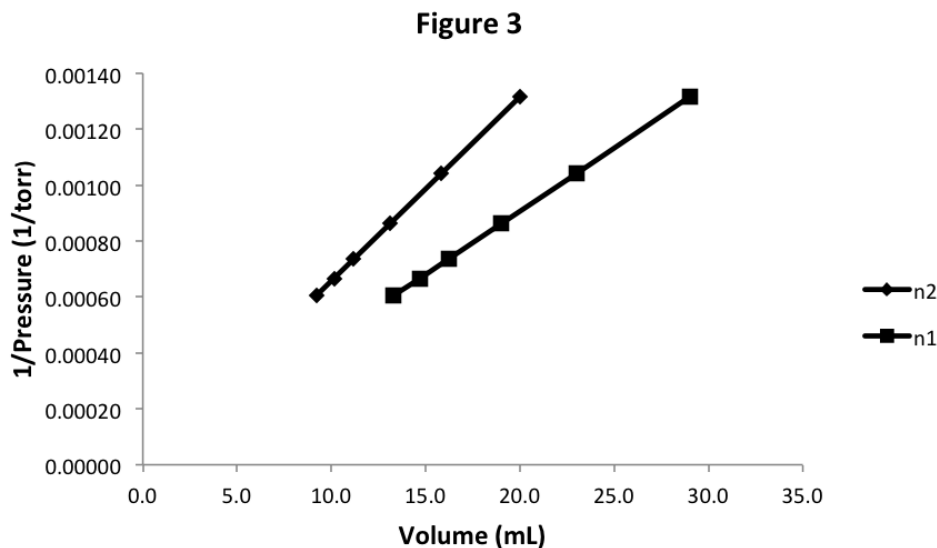
This also means that the pressure must simply be a constant, k, multiplied by 1/V.

Of course, this result applies only to the single sample we have taken so far – we have trapped an arbitrary amount of air in our cylinder. What would happen if we trapped a different quantity of gas or if we trapped a different gas than the mixture of gases in air?

Let's start with 29 mL of N_2 at pressure 760 torr, which are the same starting conditions for our previous sample of air. As we vary the volume and measure the pressure changes, we discover that the data is, to a very high accuracy, the same. We can repeat this experiment with O_2 , Ar, Ne, H_2 , or CH_4 , and we find in each case that if we start with the same volume and pressure, the pressure-volume data does not vary. In other words, the experimental graph in Figure 2 does not depend on what gas we are studying. That is fairly surprising, since we know that the particles (atoms or molecules) of these gases have very different properties.

Let's start with 20 mL of N_2 at pressure 760 torr. We could easily determine the mass of N_2 in the cylinder and show that there is less gas than in the previous experiment. We could also apply our knowledge of Avogadro's Law and conclude that the volume of a gas is proportional to the number of particles or moles of the gas at the same pressure (and temperature). In either case, we know that we have fewer gas particles in the new sample. For this new sample, we observe that the pressure is lower at each volume, but the graph looks similar as seen in Figure 3.

Notice that we get another straight line that appears to pass through (0,0), so again the equation of this graph is $1/P = k \times V$. However, the slope of the line, or the value of k , is different. Since we changed the number of moles of gas between the two experiments, this means that the slope k is a function of the number of moles: $k(n)$. We will later determine what this function of n is.



For now, we can conclude that $1/P$ is proportional to V for each value of n . Written differently:

$$P \times V = k(n) \text{ at fixed temperature}$$

In the next section, we will see that k also depends on temperature. Thus, we conclude that the product of pressure and volume is a constant for a given amount of gas at a fixed temperature. This observation is referred to as Boyle's Law, dating to 1662.

Observation 2: Volume-Temperature Measurements on Gases

We now want to measure what happens to the pressure and volume of a sample of gas when the temperature is allowed to vary. An interesting first problem that might not have been expected is the question of how to measure temperature. In fact, for most purposes, we think of temperature only in the rather non-quantitative manner of "how hot or cold" something is. However, we measure temperature in a variety of ways that do not seem to be "hot or cold," such as by examining the length of mercury in a tube or by measuring the electrical potential across a thermocouple in an electronic thermometer. It is an important but complicated question of just what we are measuring when we measure the temperature.

Imagine that you are given a cup of water and asked to describe it as "hot" or "cold." Even without a calibrated thermometer, the experiment is simple: you put your finger in it. Only a qualitative question was asked, so there is no need for a quantitative measurement of "how hot" or "how cold" the water is. The experiment is only slightly more involved if you are given two cups of water and asked which one is hotter or colder. All we would have to do is put one finger in each cup and directly compare the differences in sensation. You still do not need a calibrated thermometer or even a temperature scale at all.

Finally, imagine that you are given a cup of water each day for a week and are asked to determine which day's cup contained the hottest or coldest water. Since you can no longer trust your sensory memory from day to day, you have no choice but to define a temperature scale. To do this, we make a physical measurement on the water by bringing it into contact with something else whose physical properties depend on the "hotness" of the water in some unspecified way. For example, the volume of mercury in a glass tube expands when placed in hot water, certain strips of metal expand or contract when heated, some liquid crystals change color when heated, and so on. We assume that this physical property will have the same value when it is placed in contact with two objects which have the same "hotness," or temperature. This allows us to make comparisons in a quantitative way, which defines the temperature measurement. Keep in mind that, when we use a thermometer to measure how "hot" or "cold" an object is, we are actually measuring a physical property which varies with how hot or cold the object is.

For simplicity, we illustrate with a mercury-filled glass tube thermometer. We observe quite easily that when the tube is inserted in water we consider "hot," the volume of mercury is larger than when we insert the tube in water that we consider "cold." Therefore, the volume of mercury is a measure of how hot something is. Furthermore, we observe that, when two very different objects appear to have the same "hotness," they also give the same volume of mercury in the glass tube. This allows us to make quantitative comparisons of "hotness" or temperature based on the volume of mercury in a tube.

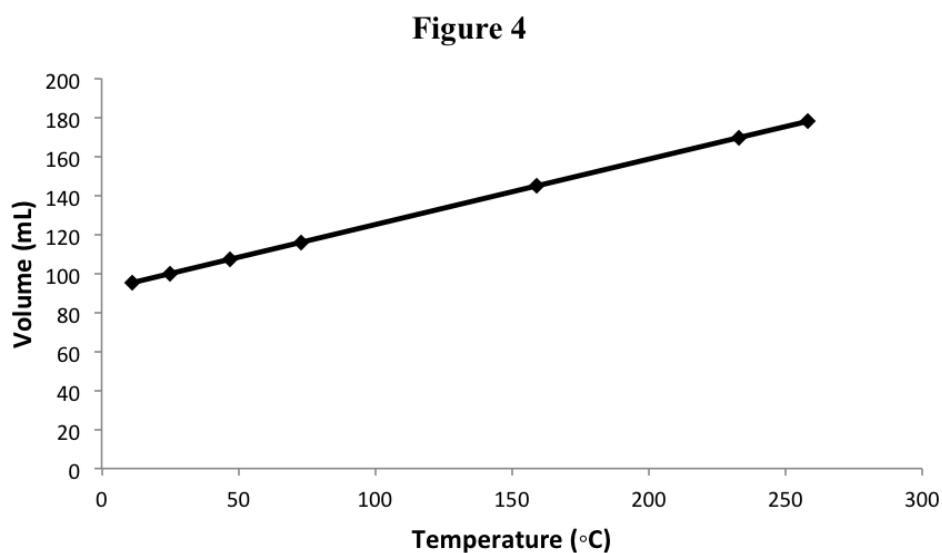
All that remains is to make up some numbers that define the scale for the temperature, and we can literally do this in any way that we please. This arbitrariness is what allows us to have two different but perfectly acceptable temperature scales, such as Fahrenheit and Centigrade. The latter scale simply assigns zero to be the temperature at which water freezes at atmospheric pressure. We then insert our mercury thermometer into freezing water, and mark the level of the mercury as "0". Another point on the Centigrade scale assigns 100 to be the boiling point of water at atmospheric pressure. We insert our mercury thermometer into boiling water and mark the level of mercury as "100." Finally, we just mark off in increments of 1/100 of the distance between the "0" and the "100" marks, and we have a working thermometer. Given the arbitrariness of this way of measuring temperature, it is not all obvious what physical property we are measuring, and as such it would be remarkable to find a quantitative relationship between temperature and any other physical property.

Yet that is what we now observe for volumes and pressures of gases. We take the same syringe used in the previous experiment and trap in it a small sample of air at room temperature and atmospheric pressure. (From our observations above, it should be clear that the type of gas we use is irrelevant since the pressure and volume relationship is the same for all gases.) The experiment consists of measuring the volume of the gas sample in the syringe as we vary the sample's temperature, which is measured by a mercury thermometer. In each measurement, the pressure of the gas is held fixed by allowing the piston in the syringe to move freely against atmospheric pressure. A sample set of data is shown in Table 3 and plotted in Figure 4.

Temperature (°C)	Volume (mL)
11	95.3

25	100.0
47	107.4
73	116.1
159	145.0
233	169.8
258	178.1

Sample Data from Volume-Temperature Measurement



This is an amazingly simple relationship. The volume of the gas at fixed pressure correlates exactly with the volume of the mercury in the glass cylinder, both of which correlate with the temperature. There is a simple linear (straight line) relationship between the volume of a sample of gas and its temperature. We can express this in the form of an equation for a line:

$$V = \alpha t + \beta$$

where V is the volume and t is the temperature in $^{\circ}\text{C}$. A and B are the slope and y-intercept of the line, respectively. For this sample of gas at this temperature, our measurements give us $A = 0.335 \text{ mL}/^{\circ}\text{C}$ and $B = 91.7 \text{ mL}$.

These numbers alone don't mean much to us, because these are the specific numbers for a specific amount of gas at a specific pressure. But we can rewrite this equation in a slightly different form:

$$V = \alpha (t + \beta/\alpha)$$

This is the same equation, except that it reveals that the quantity β/α must be a temperature, since we can add it to a temperature and it has units of temperature. If we extrapolated the straight line in Figure 4 all the way to the x-axis, we find that the x-intercept of the graph, or the quantity $-\beta/\alpha$ equals -273°C . At that temperature, the volume of the gas would be expected to be zero. This assumes that the equation can be extrapolated to that temperature. This is quite an overly optimistic extrapolation, since we haven't made any measurements anywhere near to -273°C . In fact, our gas sample would condense to a liquid or solid before we ever reached that low of a temperature.

We know that the volume of a gas sample depends on the pressure and the amount of gas in the sample. This means that the values of α and β also depend on the pressure and amount of gas and carry no particular significance. However, when we repeat our observations for many values of the amount of gas and many values of the fixed pressure, we find a wonderful result: the ratio $-\beta/\alpha = -273^{\circ}\text{C}$ does not vary from one sample to the next. Every set of observations produces a graph like Figure 4 with a straight line that extrapolates to an x-intercept of -273°C .

Although we do not yet know the physical significance of this exact temperature, we can assert that it is a true constant, independent of any choice of the conditions of the experiment. We refer to this temperature as "absolute zero," since a temperature below this value would be predicted to produce a negative gas volume. Evidently, then, we cannot expect to lower the temperature of any gas below -273°C .

One immediate consequence of this observation is that it provides us an “absolute temperature scale” with a zero that is not arbitrarily defined. Since

$$V = \alpha (t + \beta/\alpha)$$

then the gas volume is proportional to $t + \beta/\alpha$ where t is in $^{\circ}\text{C}$. This means it would be useful to define a temperature scale $T = t + \beta/\alpha = t + 273$. This new scale is called the absolute temperature scale and the units are in Kelvin (K). Note that the size of the unit K is the same as the size of the unit $^{\circ}\text{C}$; for example, the temperature change of 1 K between 373 K and 374 K is the same as the temperature change of 1 $^{\circ}\text{C}$ between 100 $^{\circ}\text{C}$ and 101 $^{\circ}\text{C}$.

In this new temperature scale, $V = \alpha T$. This means that the volume is proportional to the absolute temperature in Kelvin, provided that the pressure and amount of gas are held constant. This result is known as Charles’ Law, dating to 1787.

We can see this result in the data in Table 4, which are now recalibrated to the absolute temperature scale, and in Figure 5.

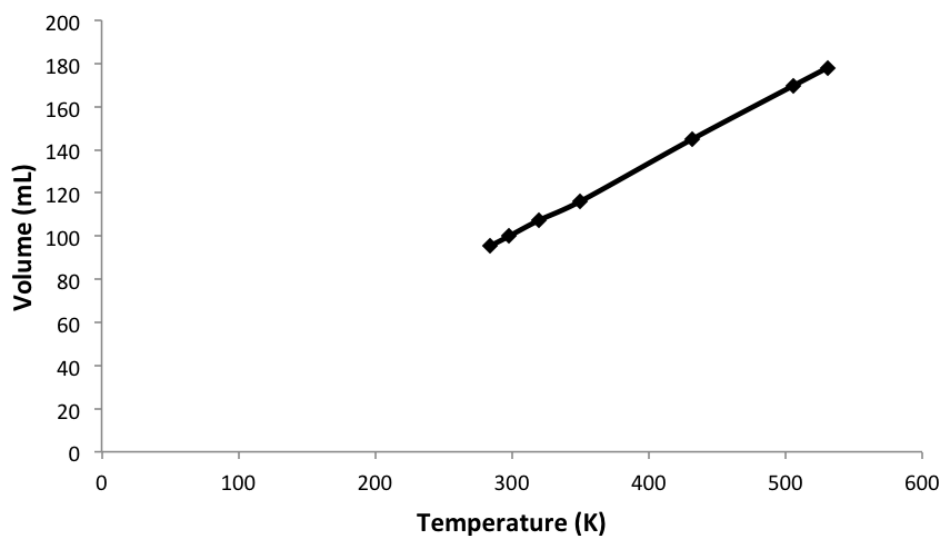
Table 4

Temperature ($^{\circ}\text{C}$)	Temperature (K)	Volume (mL)
11	284	95.3
25	298	100.0
47	320	107.4
73	350	116.1

159	432	145.0
233	506	169.8
258	531	178.1

Analysis of Volume-Temperature Data in Table 3

Figure 5



As with Boyle's Law, we must now note that the "constant" α is not really constant, since the volume also depends on the pressure and quantity of gas. Also as with Boyle's Law, we note that Charles' Law does not depend on the type of gas on which we make the measurements, but rather it depends only the number of particles of gas. Therefore, we slightly rewrite Charles' Law to explicitly indicate the dependence of α on the pressure and number of particles of gas:

$$V = \alpha(N,P) T$$

The Ideal Gas Law

We have been measuring four properties of gases: pressure, volume, temperature, and “amount,” which we have assumed above to be the number of particles through Avogadro’s Law. The results of three observations relate these four properties pairwise. Boyle’s Law relates the pressure and volume at constant temperature and amount of gas:

$$P \times V = k_B(N,T)$$

where we have given the Boyle’s Law function the name k_B (B is for Boyle) to distinguish it from other k ’s we might encounter.

Charles’ Law relates the volume and temperature at constant pressure and amount of gas:

$$V = k_C(N,P) T$$

where we have given the Charles’s Law function the name k_C (C is for Charles) to distinguish it.

Finally, the Law of Combining Volumes leads to Avogadro’s Law that the volume of a gas is proportional to the number of particles (N) provided that the temperature and pressure are held constant. If we let k_A (A is for Avogadro) be the proportionality constant between V and N, then C is a function of P and T. We can express this as

$$V = k_A(P,T) N$$

We will demonstrate below that these three relationships can be combined into a single equation relating P, V, T, and N. Jumping to the conclusion, however, we can more easily show that these three relationships can be considered as special cases of the more general equation known as the Ideal Gas Law:

$$PV = nRT$$

where R is a constant, n is the number of moles of gas, related to the number of particles N by Avogadro’s number, N_A :

$$n = N/N_A$$

In Boyle's Law, we examine the relationship of P and V when n (or N) and T are fixed. In the Ideal Gas Law, when n and T are constant, nRT is constant, so the product PV is also constant. Therefore, Boyle's Law is a special case of the Ideal Gas Law. If n and P are fixed in the Ideal Gas Law, then $V = (nR/P) T$ and nR/P is a constant. Therefore, Charles' Law is also a special case of the Ideal Gas Law. Finally, if P and T are constant, then in the Ideal Gas Law, $V = (RT/P) n$ and the volume is proportional the number of moles or particles. Hence, Avogadro's Law is a special case of the Ideal Gas Law.

We have now shown that the each of our experimental observations is consistent with the Ideal Gas Law. We might ask, though, how did we get the Ideal Gas Law? We would like to derive the Ideal Gas Law from the three experimental observations. To do so, we need to learn about the functions $k_A(N,T)$, $k_B(N,P)$, and $k_C(P,T)$.

We begin by examining Boyle's Law in more detail: if we hold N and P fixed in Boyle's Law and allow T to vary, the volume must increase with the temperature in agreement with Charles' Law. In other words, with N and P fixed, the volume must be proportional to T . Therefore, k in Boyle's Law must be proportional to T :

$$k_B(N,T) = k_{B2}(N) \times T$$

where k_{B2} is a new function which depends only on N . The first equation above then becomes

$$P \times V = k_{B2}(N) \times T$$

Avogadro's Law tells us that, at constant pressure and temperature, the volume is proportional to the number of particles. Therefore k_{B2} must also increase proportionally with the number of particles:

$$k_{B2}(N) = k \times N$$

where k is yet another new constant. In this case, however, there are no variables left, and k is truly a constant. That is why it has no subscript to distinguish it. Combining these last two equations gives

$$P \times V = k \times N \times T$$

This is very close to the Ideal Gas Law, except that we have the number of particles, N , instead of the number of moles, n . We put this result in the more familiar form by expressing the number of particles in terms of the number of moles, n , by dividing the number of particles by Avogadro's number, N_A :

$$n = N / N_A$$

Then, from above,

$$P \times V = k \times N_A \times n \times T$$

The two constants, k and N_A , are usually combined into a single constant, which is commonly called R , the gas constant. This produces the familiar conclusion:

$$PV = nRT$$

Observation 3: Partial Pressures

We briefly referred above to the pressure of mixtures of gases, noting in our measurements leading to Boyle's Law that the total pressure of the mixture depends only on the number of moles of gas, regardless of the types and amounts of gases in the mixture. The Ideal Gas Law reveals that the pressure exerted by a mole of molecules does not depend on what those molecules are, and our earlier observation about gas mixtures is consistent with that conclusion.

We now examine the actual process of mixing two gases together and measuring the total pressure. Consider a container of fixed volume 25.0 L. We inject into that container 0.78 moles of N_2 gas at 298 K. From the Ideal Gas Law, we can easily calculate the measured pressure of the nitrogen gas to be 0.763 atm. We now take a second identical container of fixed volume 25.0 L, and we inject into that container 0.22 moles of O_2 gas at 298 K. The measured pressure of the oxygen gas is 0.215 atm. As a third measurement, we inject 0.22 moles of O_2 gas at 298 K into the first container which

already has 0.78 moles of N_2 . (Note that the mixture of gases we have prepared is very similar to that of air.) The measured pressure in this container is now found to be 0.978 atm.

We now note that the total pressure of the mixture of N_2 and O_2 in the container is equal to the sum of the pressures of the N_2 and O_2 samples when each was taken separately. This is an interesting result, because it says that each gas in the mixture exerts the pressure it would exert if it were the only gas present. In the next study, we will see that this observation gives us a lot of insight into what the gas particles are doing.

We now define the “partial pressure” of each gas in the mixture to be the pressure of each gas as if it were the only gas present. Our measurements tell us that the partial pressure of N_2 , P_{N_2} , is 0.763 atm, and the partial pressure of O_2 , P_{O_2} , is 0.215 atm. Note that this definition of the partial pressure means that the partial pressure of each component can be calculated from the Ideal Gas Law. For example:

$$P_{\text{O}_2} = n_{\text{O}_2}RT/V \text{ and } P_{\text{N}_2} = n_{\text{N}_2}RT/V$$

With this definition, we can now summarize our observation by saying that the total pressure of the mixture of oxygen and nitrogen is equal to the sum of the partial pressures of the two gases. This is a general result described by Dalton’s Law of Partial Pressures: the total pressure of a mixture of gases is the sum of the partial pressures of the component gases in the mixture.

In some sense, this is not a surprising outcome. We knew from our measurements that the pressure of a gas did not depend on the type of gas, but instead depended on the number of gas particles. It makes sense, then, that we can calculate the total pressure of a gas by summing up the numbers of moles of each gas present and using that total number of moles in the Ideal Gas Law to predict the pressure.

Review and Discussion Questions

1. Sketch a graph with two curves showing Pressure vs. Volume for two different values of the number of moles of gas, with $n_2 > n_1$, both at the same temperature. Explain the comparison of the two curves.
2. Sketch a graph with two curves showing Pressure vs. $1/\text{Volume}$ for two different values of the number of moles of gas, with $n_2 > n_1$, both at the same temperature. Explain the comparison of the two curves.
3. Sketch a graph with two curves showing Volume vs. Temperature for two different values of the number of moles of gas, with $n_2 > n_1$, both at the same pressure. Explain the comparison of the two curves.
4. Sketch a graph with two curves showing Volume vs. Temperature for two different values of the pressure of the gas, with $P_2 > P_1$, both for the same number of moles. Explain the comparison of the two curves.
5. Explain the significance of the fact that, in the volume-temperature experiments, β/α is observed to have the same value, independent of the quantity of gas studied and the type of gas studied. What is the significance of the quantity β/α ? Why is it more significant than either β or α ?
6. Amonton's Law says that the pressure of a gas is proportional to the absolute temperature for a fixed quantity of gas in a fixed volume. Thus, $P = k(N,V)T$. Demonstrate that Amonton's Law can be derived by combining Boyle's Law and Charles' Law.
7. Using Boyle's Law in your reasoning, demonstrate that the "constant" in Charles' Law, i.e. $k_C(N,P)$, is inversely proportional to P .
8. Explain how Boyle's Law and Charles' Law may be combined to the general result that, for constant quantity of gas, $P \times V = k T$.
9. Using Dalton's Law and the Ideal Gas Law, show that the partial pressure of a component of a gas mixture can be calculated from $P_i = P X_i$ Where P is the total pressure of the gas mixture and X_i is the "mole fraction" of component i , defined by $X_i = n_i/n_{\text{total}}$
10. Dry air is 78.084% nitrogen, 20.946% oxygen, 0.934% argon, and 0.033% carbon dioxide. Determine the mole fractions and partial pressures of the components of dry air at standard pressure.
11. Assess the accuracy of the following statement: *Boyle's Law states that $PV = k_1$, where k_1 is a constant. Charles' Law states that $V = k_2 T$, where k_2 is a constant. Inserting V from Charles' Law into Boyle's Law results in $P k_2 T = k_1$. We can rearrange this to read $PT = k_1/k_2 = \text{a constant}$. Therefore, the pressure of a gas is inversely proportional*

to the temperature of the gas. In your assessment, you must determine what information is correct or incorrect, provide the correct information where needed, explain whether the reasoning is logical or not, and provide logical reasoning where needed.

The Kinetic Molecular Theory

Introduction

Our understanding of the bonding between atoms in molecules tells us a great deal about the structures and properties of molecules. We can use the valence shell model of atoms and the Lewis model of bonding to explain and even predict what types of molecules will be stable, like CH_4 , and which are not expected to exist, like CH_5 . This is very powerful and quite beautiful. It means that the enormous number of known substances generally fit a fairly simple set of rules that describes their molecules. Without these rules, we would be lost trying to understand the properties of the more than 50 million different substances that chemists have identified. With these rules, though, we cannot only understand the properties of each molecule but even predict the properties of other molecules even if they have never been created before.

Chemistry, though, is about changes in matter. How do substances react with one another? If a molecule is stable under ordinary conditions, why does it become unstable when the temperature is raised or other molecules are added to the flask? We are interested in chemical reactions, but we are also interested in some physical changes which take place in matter. What happens when a substance changes from solid to liquid or liquid to gas? Why do some substances do this so readily?

Answering these questions often requires us to understand how the properties of individual molecules create the properties we see in large quantities of a substance. This seems like a very challenging problem. It is hard enough to think of the structure of one molecule and try to visualize how its structure creates properties such as dipole moments or intermolecular forces. It seems much harder to imagine thinking of a mole of these molecules all interacting with each other at the same time.

We need a way to relate macroscopic properties to molecular properties. As simple examples, let's compare the substances water, carbon dioxide, and nitrogen. Each of these is composed of molecules with just a few atoms, and all of the atoms have rather small masses, so the molecules all have low

molecular weights. These three molecules have very similar molecular properties; however, the physical properties of these three substances are very different. Carbon dioxide and nitrogen are gases at room temperature, but water is a liquid up to 100 °C. We can only get nitrogen to condense by cooling it to -196 °C. This means that the boiling temperatures of water and nitrogen are different by almost 300 °C. Water is a liquid over a rather large temperature range, freezing at 0 °C and boiling at 100 °C. Nitrogen is very different – it is only a liquid between -210 °C and -196 °C. Carbon dioxide is even more interesting. At normal atmospheric pressure, carbon dioxide gas cannot be condensed into a liquid at all, no matter how cold we make it. If we keep cooling carbon dioxide gas to -60 °C, it converts directly to solid “dry ice.” We cannot melt dry ice either. Warming dry ice above -60 °C does not produce any liquid, but instead the solid “sublimes,” meaning that it converts directly into gas.

Why should these materials, whose molecules do not seem all that different, behave so differently? What are the important characteristics of these molecules that produce these physical properties?

One of our first efforts at making a connection between molecular properties and macroscopic properties is the development of the Kinetic Molecular Theory. Among the very most important concepts in Chemistry is that atoms and molecules are constantly moving. These movements have a lot to do with how and when the atoms and molecules react with each other. Also among these very important concepts is that the movements of atoms and molecules are related to their temperature. We shall see that a higher temperature corresponds to faster molecules with more energy. Knowing this will help us understand a lot of Chemistry, including how chemical reactions are affected by temperature and energy.

Foundation

Since we wish to relate macroscopic properties to molecular properties, it is worth remembering what observations and conclusions we have already made about each type of property. In this study, we will focus mainly on the observations of gases which led us to the Ideal Gas Law. We will assume that we have made measurements of the pressure of a gas under different

conditions. From these, we know that the pressure of a fixed sample of gas is inversely proportional to the volume in which the gas is contained, meaning that if we reduce the volume of the gas by compressing it, the pressure will rise. In a similar way, we know that the pressure of a fixed sample of gas in a fixed volume will increase in proportion to the temperature, provided that we measure the absolute temperature in Kelvin. And finally, the pressure of the gas kept at fixed temperature is proportional to the “particle density” of the gas, which is the number of gas particles (atoms or molecules) divided by the volume of the container.

We have also learned a great deal about molecular properties that will be useful in this Concept Development Study. We know that different atoms have different electronegativities and that, as a result, when these atoms are bonded together, the electron pair sharing is not equal. This can cause the molecule to have a molecular dipole moment. We also know about the geometries of molecules and that a symmetric molecule may not have a dipole moment even if the bonds in the molecule are polar.

There are a few results from Physics which are important to our work. The first of these is that pressure P is the force exerted F divided by the area A on which it is exerted:

$$P = \frac{F}{A}$$

This sounds complicated but is actually commonly observed. Think of the differences you see when force is applied to a small area, like the head of a nail, instead of being applied over a large area. For example, a stack of books piled on a desk creates a downward force due to gravity, but that force is applied over a large area, which is the size of the bottom book in the stack. This means that it does not generate that much pressure, so the books have no effect on the desk. However, if the stack of books is somehow piled on top of a sharp nail, the pressure created is very high because the force of gravity has been applied to a very, very small area, namely the point of the nail. This high pressure means that the nail may penetrate the surface of the desk. The force applied in either case is the same, but the pressure is quite different when the stack of books is placed on the nail.

$$F = ma$$

The second Physics concept we need has to do with force. When a force is applied to an object, the object will accelerate unless there is another equal force to offset it. The acceleration is measured as a change in either the speed of the object or its direction or both. The amount of acceleration depends on the mass of the object: the heavier the object, the less it accelerates. Newton's law tells us that the force F applied to an object is equal to the acceleration of the object a times its mass m :

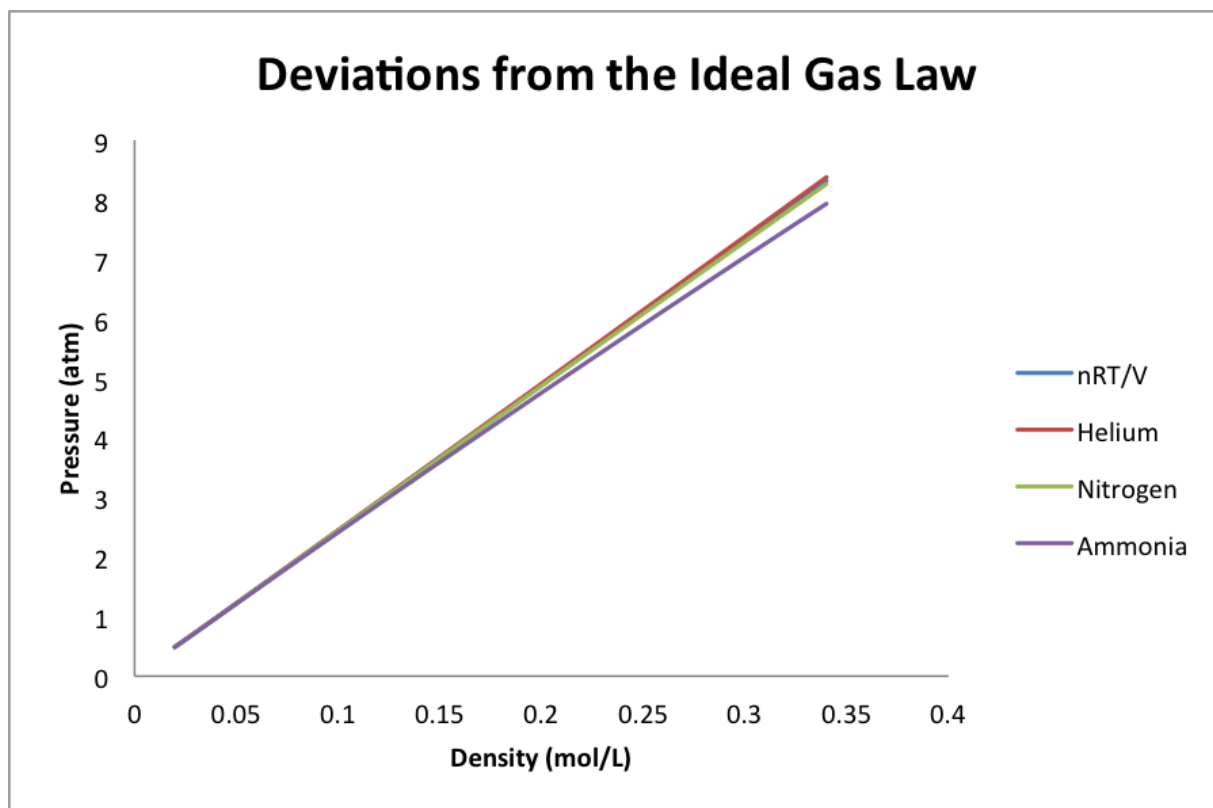
Using these two equations, we will be able to relate the pressure of a gas to the mass of the gas particles and their acceleration when they hit the walls of the container. This means that, in principle, we should be able to find the pressure of a gas from the properties and movements of the gas particles. However, in a typical sample of a gas there might be a mole or many moles of particles. Understanding the motions of 10^{23} or more molecules will require some interesting observations and some very careful thinking about how to interpret these observations.

Observation 1: The Limitations of the Ideal Gas Law

One of the amazing things about the Ideal Gas Law is that it predicts exactly the same pressure for every type of gas. If we know the temperature of the gas, the volume it is contained in, and the number of moles of the gas, then we can predict its pressure without even knowing what type of gas we have. This is very surprising. We know about the structure and bonding of molecules and we know some of the properties of molecules that the structure and bonding create. These properties vary a lot from one molecule to the next. In the Foundations, we learned that the pressure of a gas must be somehow related to the movement of the gas particles. It would seem that different molecules would move differently and this would cause different pressures. But this is not the case.

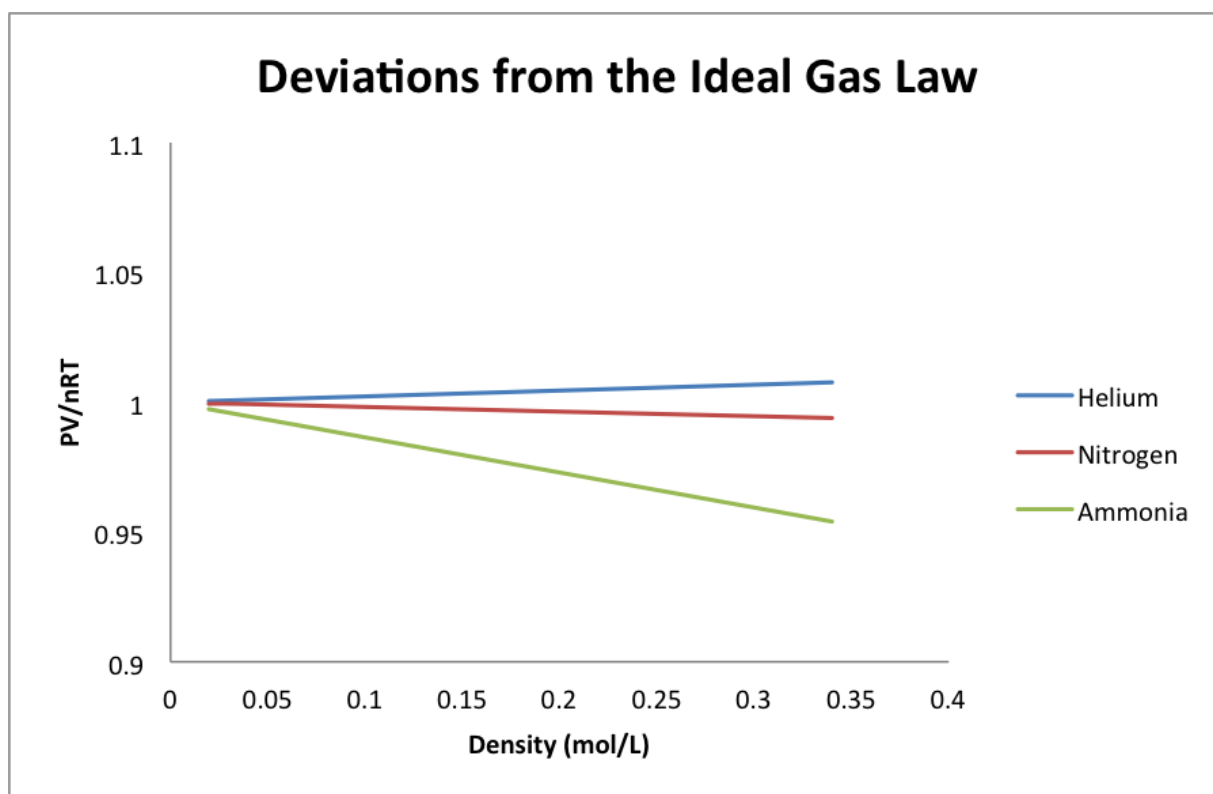
This suggests that we should look for experimental conditions where the pressures of different gases are different. In other words, we need to find conditions where the predictions of the Ideal Gas Law aren't correct. If we can find such conditions, we would find that P is no longer equal to nRT/V .

One way to do this is to plot P versus nRT/V for a gas: we can vary n , V , and T and look at how P changes. Rather than vary all three variables at the same time, we'll take a fixed T and vary the “particle density,” n/V . We can increase n/V by either pumping in more gas to increase n or by decreasing the volume of the container. Either way, we only have one variable to look at, which is the density of particles in the container. If we plot P versus nRT/V , we should get a straight line, since the Ideal Gas Law predicts that these are always equal to each other. This straight line should be exactly the same for all gases under all conditions if the Ideal Gas Law is valid. The results of such an experiment are shown in Figure 1 for three different gases.



These data show two features which should catch your eye. The first is that all three graphs look very much like the straight line predicted by the Ideal Gas Law even when we increase the density of particles by a factor of 10. Therefore, the Ideal Gas Law works really well even when we increase the density of the gas by quite a lot. The second feature, however, is that if we

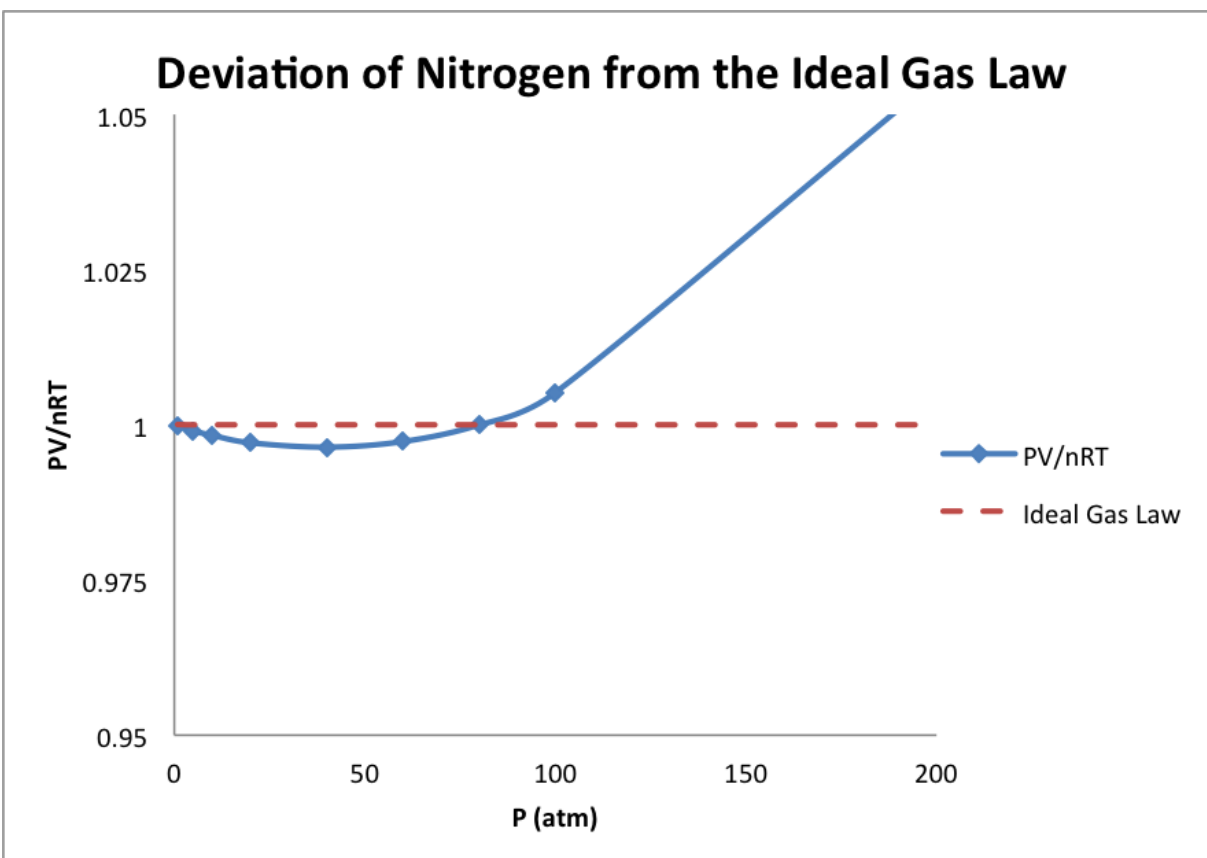
look very closely at the three graphs for the three different gases at the highest density, we see that the pressures start to vary away from the Ideal Gas Law and away from each other. This is a little hard to see in Figure 1, so we'll try plotting the data more clearly in Figure 2. This time, we will plot the ratio PV/nRT versus n/V . If the Ideal Gas Law works, then PV/nRT should always be equal to 1. If not, PV/nRT will be something different than 1, either higher or lower. This means that measuring PV/nRT in an experiment is a way for us to tell whether the Ideal Gas Law is valid.



In Figure 2, we can now more easily see that, when the density of the gas gets high enough, the Ideal Gas Law is no longer accurate. In addition, the amount by which the Ideal Gas Law is incorrect, which we might call the “deviation” from the Ideal Gas Law, is different for each gas at high density.

If we push the density of each gas to much higher values, this deviation becomes much greater. This is shown in Figure 3 for N_2 . There are two types of deviation of Figure 3 worth studying. As we start at low density

and then increase the density, the value of PV/nRT drops below 1. Note that, just as in Figure 1, the pressure of the gas continues to increase but it increase *less* than the pressure predicted by the Ideal Gas Law. This is true of most gases and is called “negative deviation” from the Ideal Gas Law, since the pressure is not as great as expected. If we continue to increase the density of the gas, PV/nRT rises about 1, so the pressure of the gas becomes greater than the pressure predicted by the Ideal Gas Law. This is called “positive deviation” from the Ideal Gas Law. The extent of negative deviation or positive deviation is different for different gases, and the pressures at which these deviations occur differ as well, but the graph for N_2 is fairly typical in shape.



We looked at these data to find the limits of the validity of the Ideal Gas Law. From these data, we can definitely conclude that the Ideal Gas Law works quite well provided that the density of the gas n/V is not too high.

This is a very valuable conclusion but we need additional data before we can build a model for why this is true.

Observation 2: Densities of Gases and Liquids

In Figures 1 and 2, we looked at gas densities where the Ideal Gas Law is accurate. Even at what we might call “high density” in Figures 1 and 2, the density is very low if we compare it to the density of a liquid. In fact, the differences between liquids and gases are enormous. To see this, let’s look at 1.0 g of H_2O . The volume of 1.0 g of liquid water is very close to 1.0 mL. It varies somewhat with changing temperature, but not very much at all, and even just below the boiling point of water, the volume of 1.0 g of H_2O is close to 1.0 mL.

Now let’s boil that 1.0 g of liquid H_2O and let’s figure out what volume the H_2O gas can fill. From the Ideal Gas Law, we know that the volume is related to the pressure, so let’s take the pressure to be standard pressure, 1 atm. At 100 °C and 1 atm pressure, 1.0 g of water gas has a volume of 1700 mL. This means that the same molecules occupy a space which is 1700 times greater when they are in a gas instead of a liquid. This is a very large increase.

How can the molecules occupy so much more space? Perhaps the molecules increase in size by a factor of 1700 when they are gas molecules instead of liquid molecules. But this sounds strange and doesn’t fit other experimental data. The volume of the gas varies with the pressure, so the value 1700 is only valid for a pressure of 1 atm. If we take a lower pressure, the volume increases, and if we take a higher pressure, the volume decreases. It seems unlikely the molecules can change their sizes to fit the pressure. If we try the same changes in pressure for the liquid, we discover that the volume of the liquid changes by such a tiny amount that it is only observable with very careful measurements. If molecules change size with pressure changes, the volume of the liquid should change too. But it does not. We have to conclude that the huge differences in the volumes of a liquid and a gas are not a result of molecules changing size when they evaporate.

If the molecules remain the same size but occupy a much larger space, there is only one possible conclusion: the molecules in the gas must be much farther apart in the gas than in the liquid. These distances must be very large. To see this, imagine a crowded elevator completely filled with people who are elbow-to-elbow. When the door opens, imagine that they now enter a room which is 1000 times larger than the elevator. Assuming that the people spread out, think about the large distances between people in this huge room. The space between people is much larger than the size of each person. In fact, the space is so large that the sizes of the individual people become insignificant. In the crowded elevator, the sizes of the people matter. But in the open room, the distances between people are so large that the distances between people are the same whether they are adults or children.

And this must be true of molecules as well. In a gas, the spaces between molecules must be very large, so large that the size of each molecule is insignificant. If we combine this conclusion with our conclusion from Observation 1, we can begin to build a model to explain why the Ideal Gas Law works provided that the gas density is not too high. At reasonable gas densities, the molecules are so far apart that the differences in size, shape, and structure of individual molecules are unimportant.

Observation 3: Dalton's Law of Partial Pressures

An interesting observation related to the Ideal Gas Law is Dalton's Law of Partial Pressures. We observed this in the previous Concept Development Study. Dalton's Law described the pressure of a mixture of gases. Let's say we mix oxygen and nitrogen, as in our atmosphere, and let's take them in the same approximate proportions as in our atmosphere. In a container of fixed volume, we can put in enough nitrogen to create a pressure of 0.8 atm. We could also put in enough oxygen to create a pressure of 0.2 atm. If we take that same amount of nitrogen and that same amount of oxygen and put them both in the same fixed volume container, we find that the pressure is 1.0 atm. In other words, the total pressure of the gas is equal to the sum of the individual pressures of the gases, called the "partial pressures."

This observation tells us that the oxygen molecules create the same 0.2 atm pressure whether the nitrogen molecules are present or not. And the same is true of the nitrogen molecules, which create a pressure of 0.8 atm whether or not the oxygen molecules are present. This is a striking observation. It means that the oxygen molecules in a mixture with nitrogen molecules must move in exactly the same way that they would if the nitrogen molecules were not there. It appears from our observations that the motions of the nitrogen molecules and the oxygen molecules do not affect each other at all.

We need to think about why this would be true. If we add this conclusion to the conclusions of Observations 1 and 2, we can see that the molecules in a gas are very far apart from one another and they do not affect each other's movements. This makes sense: if the molecules are so far apart from one another, then they never affect each other. More specifically, they never (or almost never) exert forces on each other or run into each other.

It is helpful to think again about the analogy of people in a large open space. If the space is large enough and people wander randomly in the space, then they will almost never chance across each other and therefore almost never interact with each other. In this case, it would not matter to any individual in the space whether the other people in the room were friendly or unfriendly, passive or aggressive. Each person would move just as if she or he were the only person in the room.

Our conclusion, then, is that the particles in a gas are so far apart from one another that they move independently of each other, with no interactions or forces between them which might have created either attractions or repulsions. We say that there are no “intermolecular forces” or “intermolecular interactions.”

Postulates of the Kinetic Molecular Theory

We are now ready to assemble a model to explain our observations in the Ideal Gas Law. Remember that we are trying to explain a macroscopic observation, in this case the pressure of a gas, using molecular properties or motions. So we capture the molecular concepts we developed in the three observations into a set of “postulates”:

- A gas consists of individual particles in constant and random motion.
- The distance (on average) between particles is very much larger than the sizes of individual particles.
- Because of the large distances between particles, the individual particles (on average) do not exert any forces on each other, so that they neither attract nor repel one another.
- The pressure of the gas is due entirely to the force of the collisions of the gas particles with the walls of the container.

Note that all of these postulates come from our analysis of experimental observations. And in turn, this model can be used to understand most of our observations of the properties of gases. With some extra work and additions, this model is also quite useful in understanding properties of liquids and solids as well.

The Ideal Gas Law and the Kinetic Molecular Theory

We know from our observations that the pressure of a gas decreases with volume, increases with temperature, and increases with the number of particles. To complete our connection between molecular properties and motions and experimental observations, we need to show that the postulates above lead us to the Ideal Gas Law. Notice that our postulates don't say anything about temperature. We will have to deal with that later. First, we will show how the pressure of a gas is related to the number of particles and the volume.

A detailed derivation using Physics and Mathematics is possible, but for our purposes, we will focus on the concepts. First, we know that the pressure of the gas results from the force of collisions of the gas molecules with the walls of the container. Pressure is force divided by area, so we will focus only the force of the molecules hitting a small area, probably the surface of our pressure gauge. We can call that area A . The force F is the mass of the particles hitting the wall multiplied by the acceleration resulting from the particles hitting the wall. What is that acceleration? In the easiest case, we might imagine that a particle hitting the wall keeps all of its energy and simply changes its direction. Then the acceleration is simply the change from its speed v to the same speed in the reverse direction $-v$, so the

acceleration is proportional to $2v$ and the force of each impact is proportional to $2mv$. This makes sense: the faster the particles are moving, the greater their acceleration when they hit the wall, the greater the force they create. And the greater the mass of each particle, the greater the force of each impact.

This view must be incomplete, though. Each individual particle might create a force proportional to $2v$, but there are many particles hitting the wall, generating force, and our pressure gauge can't possibly measure each tiny impact. So we need to take a different view. The total force generated by all of these tiny impacts will be determined by how many of these impacts there are. If the particles hit the wall more often, then the force will be higher. What determines how frequently the particles hit the wall? One factor should be how dense the particles are in the container. If there are a great many particles in a small volume, then many of the particles will be near the wall and collide with it. So, the frequency of the collisions of the particles with the walls of the container should be proportional to N/V , where N is the number of particles. A second factor would be how large the area of our pressure gauge is, A . A larger surface would be proportionally more collisions. A third factor would be how fast each particle is moving. Faster particles will create more frequent collisions with the wall. Each of these factors individually makes sense.

It is important to note that we have calculated the force of each tiny impact completely independently of the force of impact of any other particles. In fact, from our postulates, we have assumed that the individual particles have no effect on each other since they are so far apart from each other. This is why we can think of the force created by the gas as coming from a huge number of collisions, each one independent of all the others.

Putting these factors together, the frequency of collisions should be proportional to $(N/V)Av$. If we multiply this by the force of each collision, the total force impacted will be proportional to $(2mv)(N/V)Av$. Finally, the pressure is the force per area, so we wind up with the result that pressure P must be proportional to $2mv^2N/V$, or:

$$P = \frac{kNm v^2}{V}$$

(k is just some proportionality constant which we will need to find. We dropped the 2 since it is just a proportionality constant too.)

This result is very promising. It says that P is proportional to the number of particles N , which we could also write as the number of moles, n . That agrees with the Ideal Gas Law. It also says that P is inversely proportional to V . That also agrees with the Ideal Gas Law.

But there are two ways in which this equation looks different from the Ideal Gas Law. The first is that temperature is missing. This is because there was nothing in our postulates about temperature because we had no experiments which told us about how temperature affects molecular motion. The second is the appearance of the term mv^2 . From Physics, this is a very familiar expression, since the kinetic energy of a particle of mass m moving with speed v is $\frac{1}{2} mv^2$. Notice that the pressure is proportional to the kinetic energy of the particles.

It is hard to solve the first concern. Temperature as we measured it in the previous Concept Development Study is an arbitrary measure of hot and cold. We simply observed that this measure turned out to be proportional to the pressure of an ideal gas. However, if we compare our equation to the Ideal Gas Law, we can make progress. The Ideal Gas Law tells us that pressure is proportional to n/V times the temperature T . Our equation above tells us that pressure is proportional to N/V times the kinetic energy of the particles, $\frac{1}{2} mv^2$. This tells us that the temperature T is proportional to the kinetic energy of each particle, $\frac{1}{2} mv^2$.

The exact relationship derived mathematically shows that the temperature T is actually proportional to the average kinetic energy of the gas particles, since the particles don't all have the same speed. The complete result gives this relationship as

$$KE = \frac{3}{2} RT$$

where KE is the average kinetic energy of the gas particles and R is the same constant, which appears in the Ideal Gas Law.

This is a wonderful result for many reasons. The relationship of temperature to molecular kinetic energy is used constantly by Chemists in interpreting experimental observations. Even though we have worked it out for a gas, it turns out that this proportionality is also valid in liquids and solids.

Analysis of the Ideal Gas Law

We can use the results of the previous section to understand many of the observations we have made about gases. For example, Boyle's Law tells us that the pressure of a gas is inversely proportional to the volume of the gas, if we have a fixed number of molecules and a fixed temperature. Our results above show us that decreasing the volume for a fixed number of molecules increases the frequency with which the particles hit the walls of the container. This produces a greater force and thus a higher pressure.

We also know that the pressure of a gas increases with the number of particles, if the volume and temperature are fixed. Our results show us again that, for a fixed volume, more particles will create more collisions with the walls, producing a greater force and a higher pressure.

Finally, we know that the pressure of a gas increases with the temperature. Our results above show that increasing the temperature increases the speed of the particles. This increases the frequency of collisions and increases the force of each collision. Therefore, the increase in pressure is proportional to v^2 .

We can also interpret the deviations from the Ideal Gas Law observed in Figures 1, 2, and 3. Remember that a gas at high density may have a greater pressure or a lower pressure than predicted by the Ideal Gas Law. But the postulates of the Kinetic Molecular Theory lead us to predictions that match the Ideal Gas Law. This means that, if the pressure of a gas under some special conditions does not match the prediction of the Ideal Gas Law, then one or more of the postulates of the Kinetic Molecular Theory must not be correct for those conditions.

We only see deviations from the Ideal Gas Law at high particle density, and in this case, the particles are much closer together on average than at lower

density. Looking back at the postulates above, this means that we can no longer assume that the gas particles do not interact with each other. If the particles do interact, they exert forces on each other, which will consequently change their speeds.

If the speeds are reduced by these forces, there will be fewer impacts with the wall, and each impact will exert a weaker force on the wall. Therefore the pressure will be lower than if the particles don't exert these forces on each other. What force between the particles would cause the speeds to be lower? If the particles attract each other, then this attraction will cause each particle to slow down as it moves towards the wall, since it will be attracted to particles behind it. We can conclude that attractions between molecules will lower the pressure, which we called a negative deviation from the Ideal Gas Law. Therefore, when we see a large negative deviation from the Ideal Gas Law, we can conclude the molecules have strong intermolecular attractions.

If the speeds are increased by the intermolecular forces, there will be more impacts with the wall and each impact will exert a great force on the wall, causing a higher pressure. Following our reasoning above, a positive deviation from the Ideal Gas Law must be due to molecules with strong intermolecular repulsions.

Our experiments tell us that, as we increase the density of the gas particles to a high value, we first see negative deviations from the Ideal Gas Law. Therefore, as we increase the density, the molecules are on average closer together and the first intermolecular force they experience is attraction. This means that the attraction of particles is important when the particles are still rather far apart from each other. Only when the particle density gets very high and the particles are on average much closer together will repulsions become important resulting in positive deviations from the Ideal Gas Law.

This analysis of experimental observations from the Kinetic Molecular Theory can be applied to understanding properties of liquids and solids. In particular, it is very helpful in understanding why substances have high or low melting or boiling points. We begin our study of these different phases of matter in the next Concept Development Study.

Review and Discussion Questions

1. Explain the significance to the development of the kinetic molecular model of the observation that the ideal gas law works well only at low pressure.
2. Explain the significance to the development of the kinetic molecular model of the observation that the pressure predicted by the ideal gas law is independent of the type of gas.
3. Sketch the value of PV/nRT as a function of density for two gases, one with strong intermolecular attractions and one with weak intermolecular attractions but strong repulsions.
4. Give a brief molecular explanation for the observation that the pressure of a gas at fixed temperature increases proportionally with the density of the gas.
5. Give a brief molecular explanation for the observation that the pressure of a gas confined to a fixed volume increases proportionally with the temperature of the gas.
6. Give a brief molecular explanation for the observation that the volume of a balloon increases roughly proportionally with the temperature of the gas inside the balloon.

Phase Transitions and Phase Equilibrium

Introduction

We have developed a very clear molecular picture of the gas phase via the Kinetic Molecular Theory. The gas particles (atoms or molecules) are very distant from one another, sufficiently so that there are no interactions between the particles. The path of each particle is independent of the paths of all other particles. We can determine many of the properties of the gas from this description; for example, the pressure can be determined by calculating the average force exerted by collisions of the gas particles with the walls of the container.

To discuss liquids and solids, though, we will be forced to abandon some of the most fundamental pieces of the Kinetic Molecular Theory of Gases. First, it is clear that the particles in the liquid or solid phases are very much closer together than they are in the gas phase, because the densities of these “condensed” phases are of the order of a thousand times greater than the typical density of a gas. In fact, we should expect that the particles in the liquid or solid phases are essentially in constant contact with each other. Second, since the particles in a liquid or solid are in close contact, it is not reasonable to imagine that the particles do not interact with one another. Our assumption that the gas particles do not interact is based, in part, on the concept that gas particles are too far apart to interact. Moreover, particles in a liquid or solid must interact, for without attractions between these particles, random motion would require that the solid or liquid dissipate or fall apart.

In this study, we will pursue a model to describe the differences between condensed phases and gases. To do so, we will begin by observing the transitions that occur between the liquid and gas phases. We will analyze the experimental conditions under which we expect to observe a substance in the liquid form or in the gas form, and we will also discover experimental conditions under which the two phases are present simultaneously. This will lead us to one of the ubiquitous concepts in Chemistry: equilibrium. By analyzing the conditions of phase equilibrium, we will develop a kinetic molecular view of liquids and of the equilibrium between a liquid and gas.

Foundation

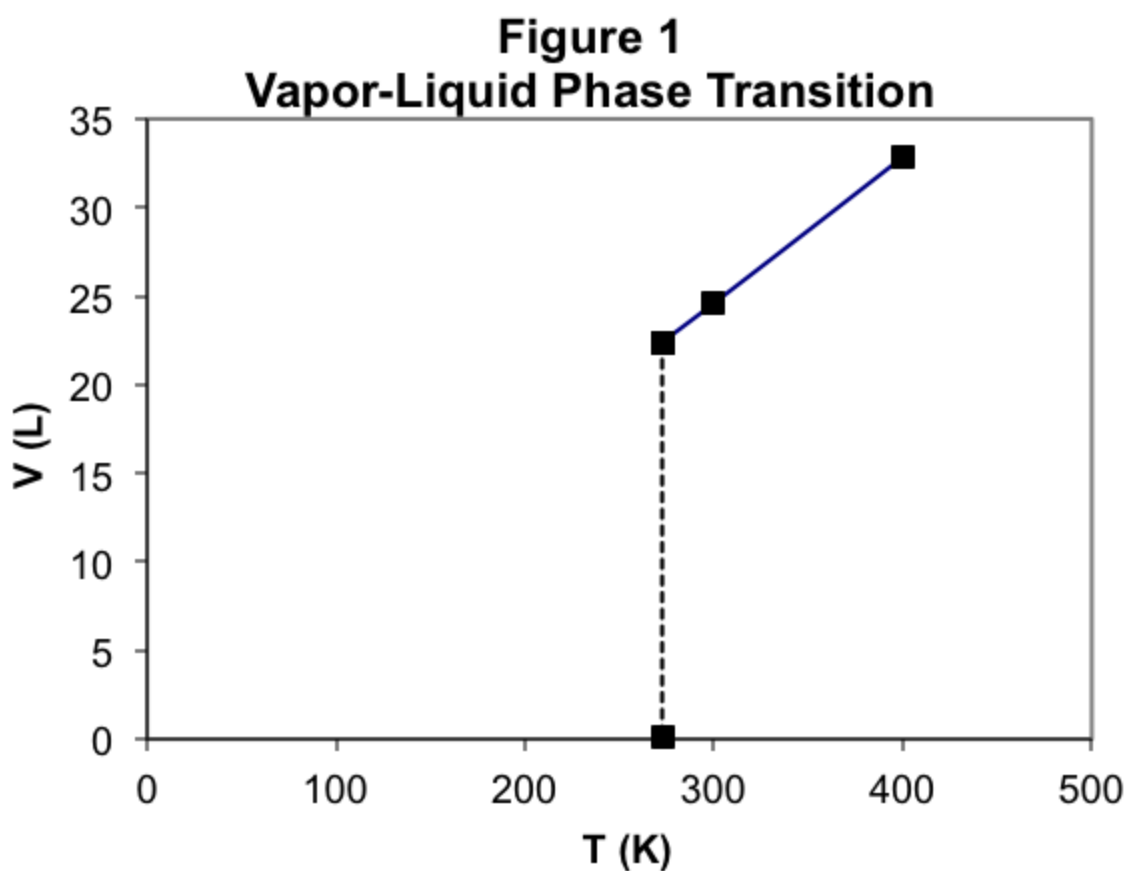
The "phase" of a substance is the particular physical state it is in. The most common phases are solid, liquid, and gas, each easily distinguishable by their significantly different physical properties. A given substance can exist in different phases under different conditions: water can exist as solid ice, liquid, or steam, but water molecules are H_2O regardless of the phase. Furthermore, a substance changes phase without undergoing any chemical transformation: the evaporation of water or the melting of ice occur without decomposition or modification of the water molecules. In describing the phase changes of a substance, we will also assume an understanding of the principles of the Atomic Molecular Theory and the Kinetic Molecular Theory.

Observation 1: Gas-Liquid Phase Transitions

We begin by returning to our observations of Charles' Law, which states that the volume of a fixed sample of a gas is proportional to the absolute temperature of the gas, provided that the pressure is held constant. Remember that we observed Charles' Law by trapping an amount of gas in a cylinder fitted with a piston and applying a fixed pressure to the piston. When we vary the temperature of the gas, the piston moves to maintain a constant pressure of the trapped gas, since the pressure applied to the piston is constant. At each temperature, the piston moves to a new point with a new total volume inside the cylinder, and we can then measure the volume of the gas. Our measurements showed that the gas volume is proportional to the absolute temperature in Kelvin. Thus, in Figure 1, a graph of the volume of 1.00 mol of butane gas (C_4H_{10}) versus its absolute temperature is a straight line, and that straight line could be extrapolated to a zero volume at 0 K.

What if we keep lowering the temperature? Do we observe the extrapolated straight line in Figure 1? To find out, we take exactly 1.00 mol of butane gas at 1 atm pressure inside our cylinder. When we start at a temperature of 400 K and slowly lower it to 300 K, we observe the expected proportional decrease in the volume from 32.8 L to 24.6 L. We also observe that this proportionality works very well for temperatures just slightly above 272.6

K, where the volume is 22.4 L. However, as shown in Figure 1, when we reach 272.6 K, the volume of the butane drops very abruptly, falling to about 0.097 L at temperatures just slightly below 272.6K. This is less than one-half of one percent of the previous volume! This striking change in volume is shown in Figure 1 as a vertical line at 272.6 K. The new volume is so small that it looks like a zero volume on the graph. Actually, the volume is non-zero, just very small in comparison to the previously measured volumes.

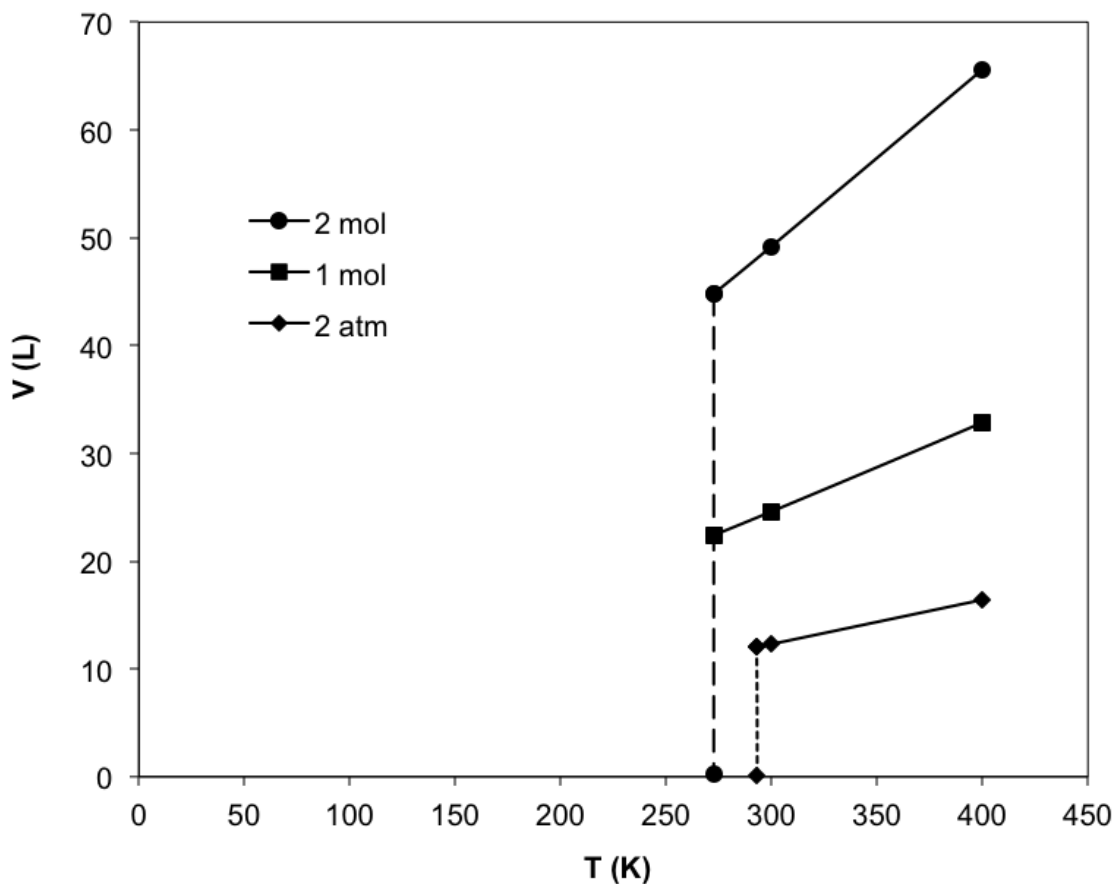


This dramatic change in physical properties at one temperature is referred to as a “phase transition.” When cooling butane through the temperature 272.6 K, the butane is abruptly converted at that temperature from one phase, gas, to another phase, liquid, with very different physical properties.

If we reverse the process, starting with liquid butane at 1 atm pressure and a temperature below 272.6 K and heat it, we find that the butane remains entirely liquid for temperatures below 272.6 K and then becomes entirely gaseous for temperatures above 272.6 K. We refer to the temperature of the phase transition by the familiar name “boiling point temperature.” (We will discuss the phases present at the boiling point, rather than above and below that temperature, in the next section.)

We now consider how the phase transition between solid and liquid depends on a variety of factors, including the amount of substance, the type of substance, and the pressure we apply. We first look at changing the amount of the substance by capturing 2.00 mol of butane in the cylinder, still at 1 atm pressure. The volume of 2.00 mol of butane is twice that of 1.00 mol, by Avogadro’s Law. The proportional volume decrease of 2.00 mol of gas is shown in Figure 2 along with the previous result for 1.00 mol. Note that the phase transition is observed to occur at exactly the same temperature, 272.6 K, even though there is double the mass of butane. Apparently, the boiling point does not depend on how much liquid or gas there is in a sample.

Figure 2
Variation of Phase Transition with Pressure

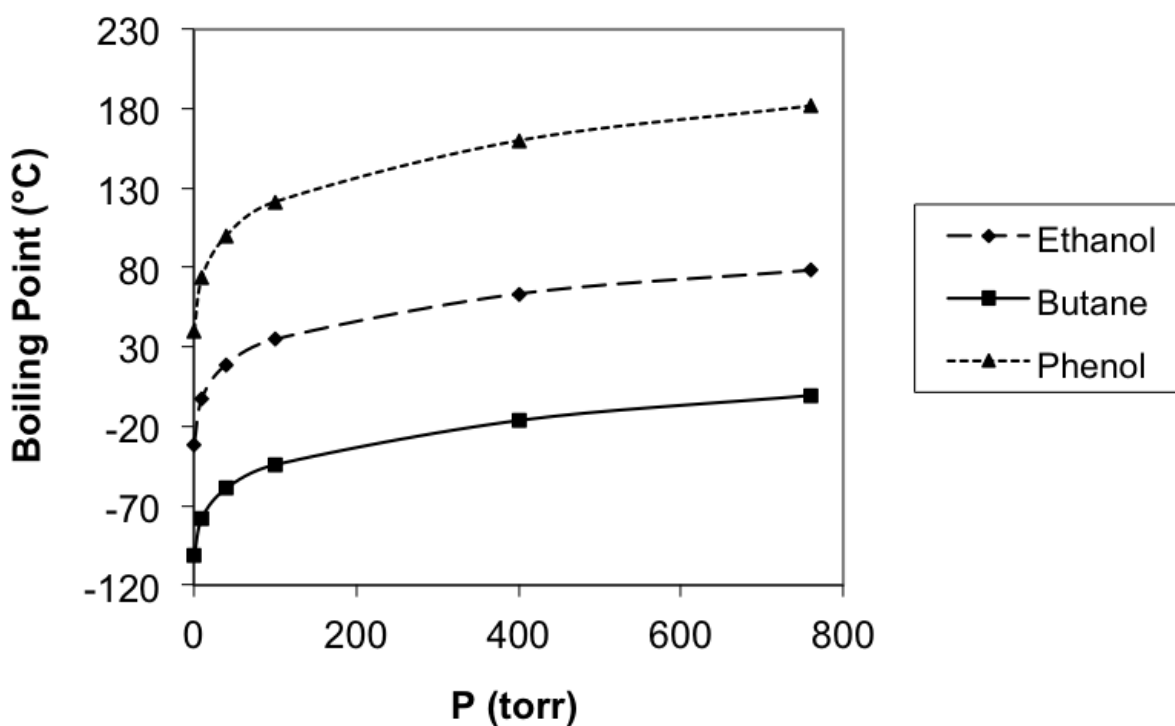


Next, let's see what happens when we vary the applied pressure by cooling 1.00 mol of butane at a constant 2.00 atm pressure, instead of 1.00 atm. The result is also shown in Figure 2 as the lowest line. We can see the now familiar phase transition with a similar dramatic drop in volume. However, in this case, we find that the phase transition occurs at 293.2 K, over 20 K higher than at the lower pressure. Clearly, the temperature of the phase transition depends on the applied pressure. We can measure the boiling point temperature of butane for many values of the applied pressure, and these results are plotted in Figure 3.

Finally, we consider varying the substance trapped in the cylinder, replacing the butane with ethanol or phenol. We discover that the boiling point

temperature depends on both the substance identity as well as on the applied pressure. As we found before, the boiling point does not depend on the amount of the substance we trap. In Figure 3, we have also plotted the boiling point as a function of the applied pressure for these three substances. It is very clear that the boiling points for different substances can be very different from one another, although the variation of the boiling point with pressure looks similar from one substance to the next.

Figure 3



Observation 2: Vapor pressure of a liquid

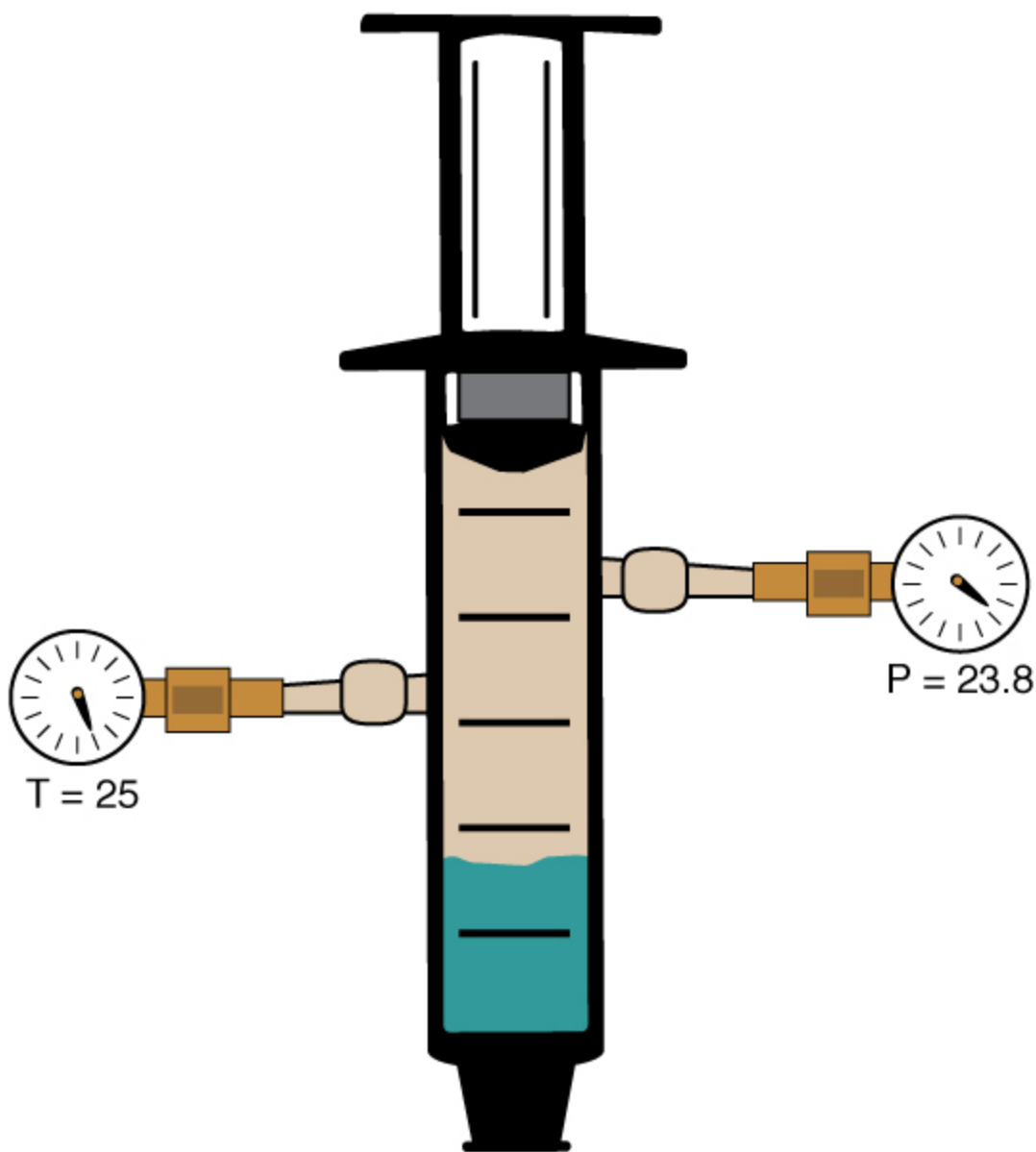
Our previous observations indicate that, for a given pressure, there is a phase transition temperature for liquid and gas: below the boiling point, the liquid is the only “stable” phase which exists, and any gas that might exist at that point will spontaneously condense into liquid. Above the boiling

point, the gas is the only stable phase and any liquid present will spontaneously evaporate.

However, it is a common observation that any liquid left in an open container will, under most conditions, eventually evaporate, even if the temperature of the liquid is well below the normal boiling point. As a simple example, puddles of water on sidewalks evaporate at air temperatures far below the 100 °C boiling point of water. This everyday observation only seems surprising in light of the discussion above. Why would liquid water spontaneously evaporate if liquid is the more stable phase below the boiling point? We clearly have more work to do to understand phase transitions, including evaporation.

The tendency of a liquid to evaporate is referred to as its “volatility”: a more volatile liquid evaporates more readily. We can make a quantitative measure of liquid volatility. We slightly modify our previous cylinder-piston apparatus by adding a gauge to measure the pressure of gas inside the cylinder. (See Figure 4 for an illustration.) We begin with liquid water only in the cylinder with an applied pressure of 1 atm at a temperature of 25 °C, well below its boiling point. We now pull back the piston by an arbitrary amount, and then we lock the piston in place, fixing the volume trapped inside the cylinder. Since we have now opened up a large cavity in the space above the liquid water, we might expect that the pressure inside the cylinder to decrease, creating a vacuum in that space. If so, we would expect that the pressure inside the cylinder is small or zero.

Figure 4



Although there was initially no gas in the container, we observe that the pressure inside the container rises to a fixed value of 23.8 torr. Clearly, there must be gaseous water in the container, since we observe a pressure inside the container. Since there was no gas initially in the container, the gas present must have come from evaporation of some of the liquid water. But not all of the liquid evaporates, since a look inside the container reveals that there is still liquid water present. Therefore, both the liquid phase and the gas phase are present at the same time in this container. This seems

incongruous from our previous observations under different conditions where we found only liquid or gas to be stable.

In this case, we say that the liquid water and the gaseous water vapor are in "phase equilibrium." The term "equilibrium" in this case indicates that neither the vapor nor the liquid spontaneously converts into the other phase. In fact, at equilibrium, we don't observe any changes in physical properties at all. The pressure of the gas remains constant, and the amount of liquid remains constant. This means that both phases are stable at equilibrium.

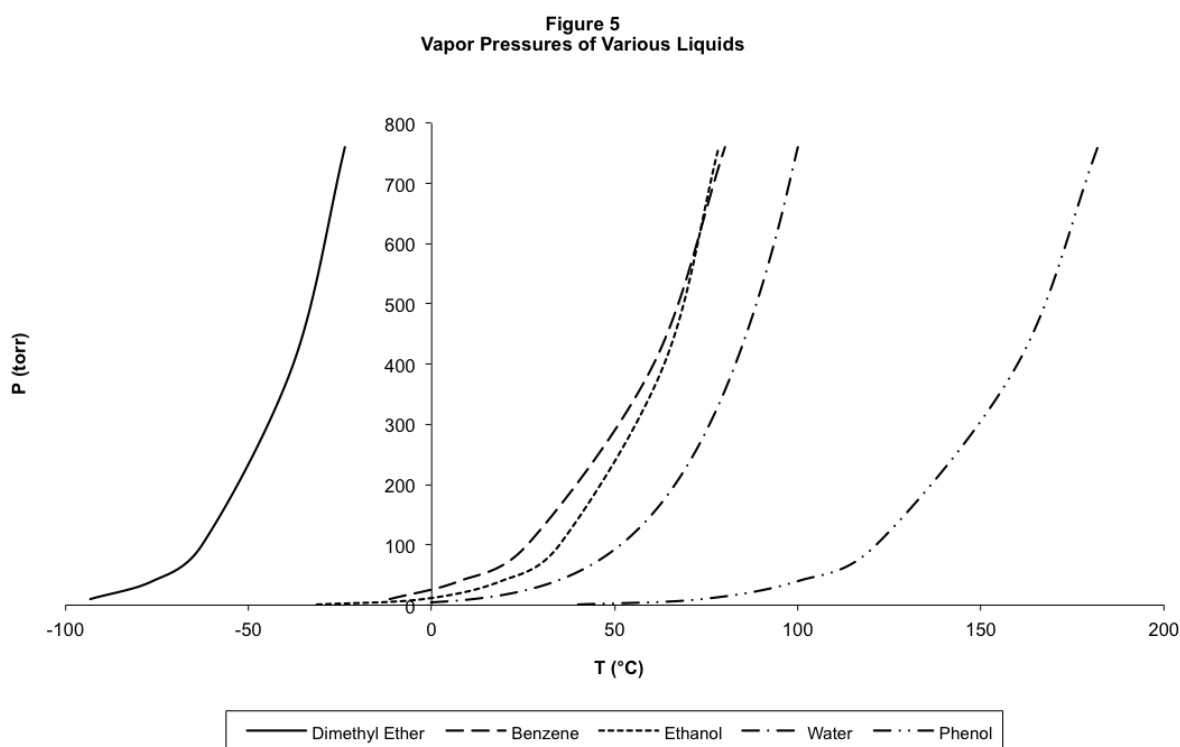
The concept of equilibrium occurs frequently in Chemistry in many different contexts. Phase equilibrium is one simple example where we can observe and understand equilibrium.

Let's see what happens to the equilibrium if we change the conditions of the experiment. We can repeat our measurement by pulling the piston back to any other arbitrary position before locking it down, trapping a different volume above the liquid. We observe that the pressure in the container in every case rises to the same fixed value of 23.8 torr, provided that there is still some liquid water present. Surprisingly, it does not matter what volume we have trapped inside the cylinder, nor does it matter how much liquid water we start with. As long as there is still some liquid water present in the cylinder at equilibrium, the pressure of the vapor above that liquid is 23.8 torr at 25 °C.

When we vary either the initial amount of liquid or the fixed volume of the container, the amount of liquid water that evaporates must be different in each case. How can we see this? The volume available for vapor to occupy is different when we either change the volume of the container or the initial volume of the liquid. Since we observe that the pressure of the vapor is the same at a fixed temperature, then the Ideal Gas Law tells us that the differing volumes correspond to differing numbers of moles of water vapor. This shows us that it is the pressure of the vapor, not the amount of vapor, which is the most important property in establishing the equilibrium between the liquid and the vapor. We can conclude that, at a fixed temperature, there is a single specific pressure at which a given liquid and its vapor will be in phase equilibrium. We call this the "vapor pressure" of the liquid.

We can make some important observations about vapor pressure. First, for a given substance, the vapor pressure varies with temperature. We can observe this by simply increasing the temperature of the closed container in the preceding experiment. In every case, we observe that the equilibrium vapor pressure always increases with increasing temperature.

The vapor pressures of several liquids at several temperatures are shown in Figure 5. The vapor pressure for each liquid increases smoothly with temperature, although the relationship between vapor pressure and temperature is definitely not proportional.



The data in Figure 5 also clearly show that the vapor pressure depends strongly on what the liquid substance is. As an example, look at the vapor pressures of these five liquids at 50 °C. The vapor pressure of phenol is tiny, whereas the vapor pressure of dimethyl ether is literally off the chart. The other three liquids have varying vapor pressures in between.

These variations in vapor pressure reflect the differing "volatilities" of the liquids: those with higher vapor pressures are more volatile, which makes sense since the liquid more readily transitions to the gaseous phase. In addition, there is a very interesting correlation between the volatility of a liquid and its boiling point. Without exception, the substances with high boiling points have low vapor pressures and vice versa. We will explore this correlation in detail in the next Concept Development Study.

Observation 3: Dynamic Equilibrium between Liquid and Gas Phases

There are several very interesting questions raised by our observations of phase equilibrium and vapor pressure. The first we will consider is why the vapor pressure at equilibrium with the liquid does not depend on the volume of the container into which the liquid evaporates. Nor does it depend on the amount of liquid in the container. Why do we always get the same pressure at equilibrium for the same temperature, regardless of other conditions? We need to understand how the vapor and liquid coexist in equilibrium. How is this equilibrium achieved?

To approach these questions, let us look again at the experimental set up in Figure 4. We begin with a container with a fixed volume containing some liquid, and equilibrium is achieved at the vapor pressure of the liquid at the fixed temperature given. When we adjust the volume to a larger fixed volume, the pressure automatically and immediately adjusts at equilibrium to exactly the same vapor pressure. This looks like magic. How is this possible?

Since the vapor exerts the same pressure in a larger volume at the same temperature, the Ideal Gas Law tells us that there are more molecules in the vapor after the volume is increased and equilibrium is reestablished. Therefore, more liquid must have evaporated to achieve this equilibrium, since the liquid is the only possible source of these extra molecules in the vapor phase. This leads us to ask how the liquid responded to the increase in overhead volume, since changing the volume presumably only affected the space in which the gas molecules move, not the liquid molecules. How did the liquid "know" to evaporate when the volume increased? We moved

the piston, but the piston was not in contact with the liquid. So the molecules in the liquid could not detect the increase in volume for the gas, and thus could not possibly be responding to that increase. Nevertheless, more liquid molecules evaporated after the volume was increased.

The only reasonable conclusion is that the molecules in the liquid were always evaporating, even before the volume of the container was increased. There must be a constant movement of molecules from the liquid phase into the gas phase at all times, whether we move the piston or not. When we fix the volume, the pressure of the gas above the liquid remains constant, so there must be a constant number of molecules in the gas phase even though evaporation is constantly occurring. For this to be true, condensation must also always be occurring, as molecules in the gas must constantly be entering into the liquid phase. If the pressure remains constant in a fixed volume, then the number of molecules entering into the gas from the liquid must be exactly offset by the number of molecules entering the liquid from the gas. The rate of evaporation must be equal to the rate of condensation at equilibrium!

At equilibrium, therefore, even though the pressure and temperature inside the container are unchanging, there is constant movement of molecules between the phases. This is called “dynamic equilibrium.” The situation is “equilibrium” in that the observable properties of the liquid and gas in the container are not changing, but the situation is “dynamic” in that there is constant movement of molecules between phases. The dynamic processes that take place offset each other exactly, so that the macroscopic properties of the liquid and gas do not change.

What are the factors that are important in this dynamic equilibrium? To find out, we examine what happens when we increase the volume of the container to a larger fixed volume. We know that the pressure at equilibrium returns to the same vapor pressure and that there are therefore more molecules in the vapor phase. How did they get there? It must be the case that when the volume is increased, evaporation initially occurs more rapidly than condensation until equilibrium is achieved. Which changed: the rate of evaporation or the rate of condensation?

In order for a molecule to leave the gas phase and enter the liquid phase, the molecule must strike the surface of the liquid. So, the rate of condensation must depend on the frequency of molecules striking the liquid surface. We can recall our calculations in the Kinetic Molecular Theory, where we found that the frequency of collisions of gas molecules with the walls of a container depends in large part on the density of the gas molecules. This means that the frequency of molecules in the gas striking the liquid surface must decrease when the volume is increased, because the density of molecules in the gas decreases when the volume increases. Increasing the volume decreases the rate of condensation, which becomes smaller than the rate of evaporation. This means that there is a net flow of molecules from liquid to gas. This continues until the density of molecules in the gas is restored from the evaporation process to its original value, at which the rate of evaporation is matched by the rate of condensation. When this happens, the gas pressure stops increasing and the pressure must be the same as it was before the volume was increased. This explains why, at a given temperature, the vapor pressure must always be the same value at equilibrium.

It is interesting that the vapor pressure does not depend on the surface area of the liquid, even though the rate at which gas molecules condense must be greater when there is more liquid surface to strike. With a constant vapor pressure for larger surface area and greater rate of condensation, it must be that the evaporation rate is also greater for a larger surface area. This makes sense and agrees with everyday observation: when a liquid is spread out over a larger area, it evaporates more quickly.

This explanation begs another question: what determines the rate of evaporation? It appears that the rate of evaporation does not change when the temperature is unchanged, so let's change the temperature. This leads us back to the experimental data in Figure 5, which shows that the vapor pressure always increases as we increase the temperature. It is important to realize that this increase is not due solely to the relationship between pressure and temperature in the Ideal Gas Law. That relationship is proportional. The pressure increases in Figure 5 are much, much larger than proportional to the temperature increases.

At higher temperature for a specific liquid, the vapor pressure increases. This means that there are more molecules in the vapor phase at the higher temperature, and as such, the rate of condensation must be higher at the higher temperature. But at equilibrium the rate of condensation must equal the rate of evaporation. This means that the rate of evaporation is also larger at the higher temperature. Furthermore, the rate of evaporation must depend on what the substance of the liquid is, since we get a different vapor pressure for each liquid, and therefore a different rate of condensation and a different rate of evaporation.

We need to develop a model that accounts for these observations, that a higher temperature must mean a higher rate of evaporation and that different substances have different rates of evaporation. We recall that for gases, temperature is a measure of the kinetic energy of the molecules. We can easily believe that the same is true for the kinetic energy of the molecules in the liquid phase. In fact, our vapor pressure data indicate that this is true, because at higher temperatures, more molecules are able to escape the liquid. The rate of evaporation must be determined by the number of molecules in the liquid that have sufficient kinetic energy to escape the intermolecular forces in the liquid. By increasing the temperature, we increase this number, so the rate of evaporation goes up. Therefore, the temperature of the liquid is a measure of the kinetic energy of the molecules in the liquid.

We are left only to understand why the rate of evaporation varies from substance to substance. For a substance with a lower vapor pressure and therefore lower rates of condensation and evaporation, it must be that that substance has fewer molecules with sufficient kinetic energy to escape the liquid at a given temperature. This strongly indicates that the forces of attraction between the molecules in the liquid are greater for that substance.

In combination, these two conclusions give us a kinetic molecular model for liquids. The molecules in the liquid are in constant motion in close proximity to each other with attractive forces between them. The strength of the attractive force depends on the type of molecule.

This model also reveals the dynamic equilibrium to us. At a given temperature, a fraction of the liquid molecules have sufficient kinetic

energy to evaporate, and this fixes the rate of evaporation. The rate of condensation must match this rate of evaporation at equilibrium, and this can only be true at a specific pressure of the gas. Therefore, at a given temperature, only a single pressure will result in phase equilibrium for that substance. As we change the substance, we change the intermolecular attractions, and this changes the rate of evaporation and therefore changes the vapor pressure at equilibrium.

In the next study, we will examine the phase equilibrium in greater detail, and in particular we will take a much closer look at these intermolecular attractions.

Review and Discussion Questions

1. We observe that, when the applied pressure is less than the vapor pressure of a liquid, all of the liquid will spontaneously evaporate. In terms of dynamic equilibrium, explain why no liquid can be present under these conditions.
2. Using arguments from the Kinetic Molecular Theory and the concept of dynamic equilibrium, explain why, at a given applied pressure, there can be one and only one temperature, the boiling point, at which a specific liquid and its vapor can be in equilibrium.
3. Using dynamic equilibrium arguments, explain why the vapor pressure of a liquid is independent of the amount of liquid present.
4. Using dynamic equilibrium arguments, explain why the vapor pressure of a liquid is independent of the volume available for the vapor above the liquid.
5. The text describes dynamic equilibrium between a liquid and its vapor at the boiling point. Describe the dynamic equilibrium between a liquid and its solid at the melting point. Using this description, explain why the melting point of a solid varies very little as the pressure increases.
6. We observed that, without exceptions, substances with high vapor pressures have low boiling points, and substances with low vapor pressures have high boiling points. Using dynamic equilibrium, explain this correlation.

Phase Equilibrium and Intermolecular Forces

Introduction

Our study of phase equilibrium between the liquid and gas phases has opened a door to a world of information about how molecules interact in a liquid. Recall that we would like to relate the properties of individual molecules to the properties of bulk samples of a substance. Our studies of the properties of gases were a little disappointing towards this goal. We found that the properties of a mole of gas molecules are the same, accurately predicted for all substances by the Ideal Gas Law except under extreme conditions. This means that the properties of individual molecules are largely irrelevant to the properties of gases.

By contrast, we now know that each liquid has a characteristic vapor pressure at each temperature and a characteristic boiling point at each pressure, and these properties differ from one substance to the next. These differences must be related to differences in the properties of the individual molecules in the liquid phase. Furthermore, we developed a model for phase equilibrium based on a dynamic view. The rate of condensation must equal to the rate of evaporation at equilibrium. And the rate of evaporation must differ from one liquid to the next and must also vary as the temperature changes. These experimental clues will help us develop a model to account for the differences in physical properties arising from differences in the attractions of individual molecules in the liquid phase.

In this study, we will further develop the concept of phase equilibrium, including solids in our discussion. We will experimentally determine the conditions under which one of the phases is the most stable and conditions under which two or all three of the phases are stable at equilibrium. We will then build a model to describe the interactions between molecules, accounting for which types of molecules have strong attractions and which have weaker attractions.

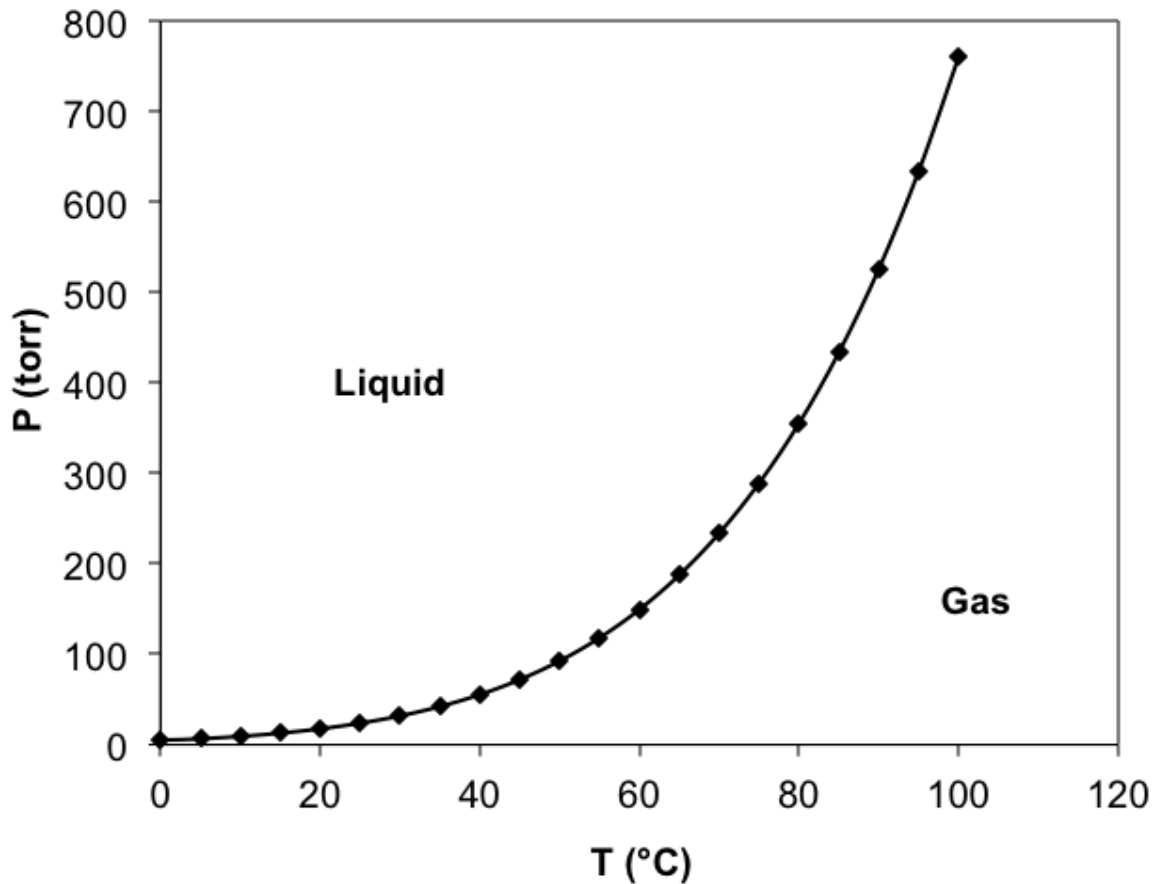
Observation 1: Liquid-Vapor Phase Diagram

In the previous study, we examined experimental data on the vapor pressures of different liquids as a function of their temperature. We found that the vapor pressure of a liquid depends strongly on what the liquid substance is. These variations reflect the differing "volatilities" of the liquids: those with higher vapor pressures are more volatile.

In addition, there is a very interesting correlation between the volatility of a liquid and the boiling point of the liquid. Without exception, the substances with high boiling points have low vapor pressures and vice versa. If we look more closely at the connection between boiling point and vapor pressure, we can find an important relationship.

Let's consider the specific case of water, with its vapor pressure given in Figure 1. We know from experiment that water boils at 1 atm pressure at 100 °C. Note in Figure 1 that, at 100 °C, the vapor pressure of water is 760 torr = 1 atm. Thus, the boiling point of water at 1 atm is the temperature at which the vapor pressure of water is equal to 1 atm. This is a general result. The boiling point of each liquid at 1 atm pressure is equal to the temperature at which the vapor pressure of that liquid is equal to 1 atm.

Figure 1
Vapor Pressure of Liquid H₂O



Let's stop to think about why this is true at 1 atm pressure. To do so, we need to remember how we observed the boiling point. We applied a pressure using a piston which trapped a liquid in a cylinder. When we elevated the temperature, we observed a phase transition at one temperature which we called the boiling point. At that point, the vapor became stable. For this to be true, the pressure created by the vapor (which is of course the vapor pressure) must at least be equal to the pressure applied externally to the piston. If the vapor pressure is less than the applied pressure, the vapor cannot resist the applied pressure, the piston moves in, and all of the vapor condenses into the liquid. Therefore, for the liquid to boil, the temperature

must be high enough for the vapor pressure to equal the applied pressure. Only at this temperature or above will the rate of evaporation be great enough to offset the rate of condensation created by the externally applied pressure.

To find the boiling point temperature at 1 atm pressure, we need to find the temperature at which the vapor pressure is 1 atm. To do so, we find the point on the graph where the vapor pressure is 1 atm and read off the corresponding temperature, which must be the boiling point. Of course, this will work at any given pressure. We just read off of Figure 1 the temperature at which the vapor pressure equals the applied pressure, and that will be the temperature at which the liquid boils at that pressure. This means that Figure. 1 gives us both the vapor pressure of water as a function of the temperature and the boiling point temperature of water as a function of the applied pressure. They are the same graph!

Remember that in the experiment, at the boiling point we observed that both liquid and gas are at equilibrium with one another. Both phases are present at the boiling point. This is true at every combination of applied pressure and boiling point temperature. Therefore, for every combination of temperature and pressure along the curve on the graph in Figure 1, we observe liquid-gas equilibrium.

What happens at combinations of temperature and pressure which are not on the line drawn in Figure 1? To find out, let's run the experiment. We first start at any temperature-pressure combination on the curve and elevate the temperature while holding the applied pressure constant. In Figure 1, this moves us to the right of the curve. We observe that all of the liquid vaporizes, and there is only gas in the container. What happened to the equilibrium? At higher temperature, the vapor pressure of the liquid rises, but if the applied pressure does not also increase, then the vapor pressure will be greater than the applied pressure. The vapor pushes back the piston and the liquid evaporates. We must therefore not be at equilibrium anymore. For all temperature and pressure combinations to the right of the curve, only vapor exists.

Now let's start at a point on the curve and lower the temperature while holding the pressure constant, leaving us to the left of the curve. We

observe that all of the gas condenses into the liquid. This is because the vapor pressure is below the applied pressure, and the piston moves in against the gas until it all condenses into the liquid. For all temperature and pressure combinations to the left of the curve, only liquid exists.

What if we start at a temperature-pressure combination on the curve and elevate the applied pressure without raising the temperature? This places us “above” the curve, which is also of course to the left of the curve. The applied pressure is now greater than the vapor pressure, and as before all of the gas will condense into the liquid. Just as before, for all points to the left of or above the curve, only liquid exists. The opposite reasoning applies if we decrease the applied pressure.

Figure 1 thus actually reveals to us what phase or phases are present at each combination of temperature and pressure: along the line, liquid and gas are in equilibrium; above or to the left of the line, only liquid is present; below or to the right of the line, only gas is present. When we label the graph with the phase or phases present in each region as in Figure 1, we refer to the graph as a “phase diagram.” In general, every substance has a liquid-vapor phase diagram like Figure 1, although the values of the pressures and temperatures along the equilibrium line differ from substance to substance.

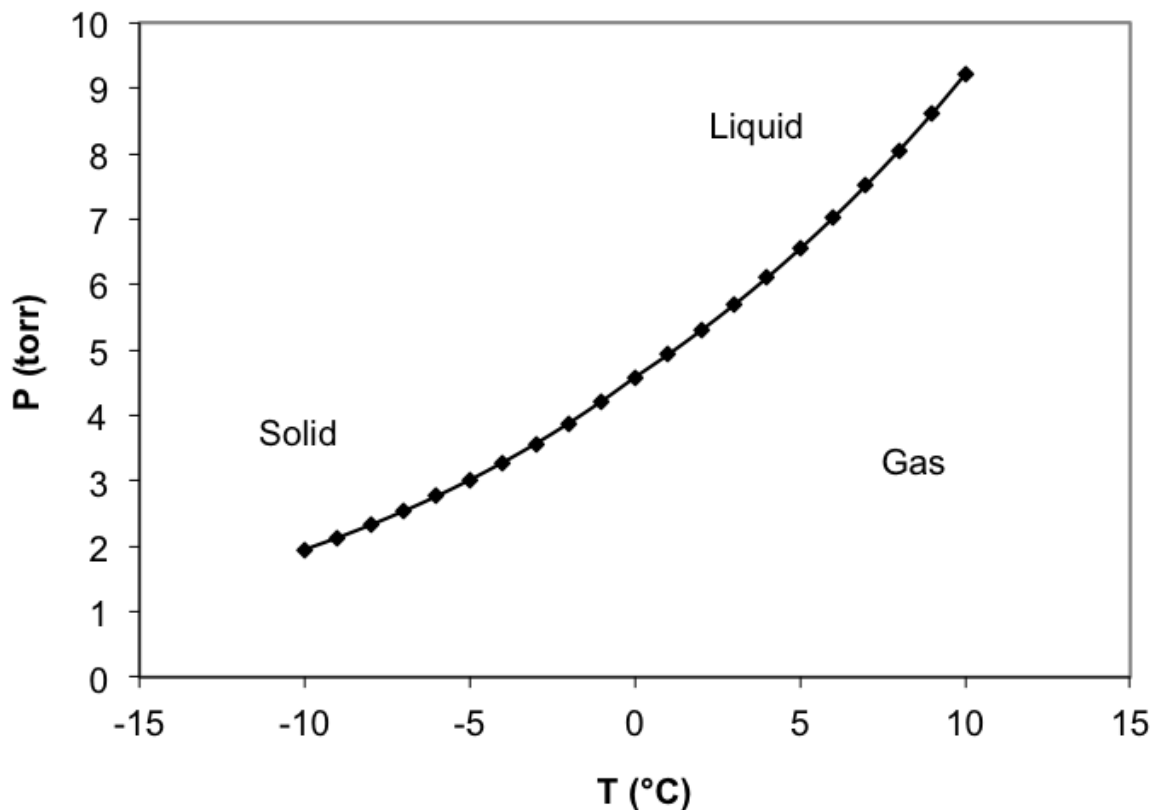
Observation 2: Solid-Liquid-Gas Phase Diagrams

Of course, Figure 1 only includes liquid, gas, and liquid-gas equilibrium. We know that, if the temperature is low enough, we expect that the water will freeze into solid. To complete the phase diagram, we need additional observations.

We go back to our apparatus we used before, with a piston in a cylinder trapping liquid water and vapor in phase equilibrium. We can start at a temperature of 25 °C and 23.8 torr since we know that this is the vapor pressure of liquid water at 25 °C. If we slowly lower the temperature, the vapor pressure decreases slowly as well, as shown in Figure 1. However, if we continue to lower the temperature, we observe an interesting transition, as shown in the more detailed Figure 2. The very smooth variation in the vapor pressure shows a slight, almost unnoticeable break very near to 0 °C.

Below this temperature, the pressure continues to vary smoothly, but along a slightly different curve.

Figure 2
H₂O Phase Transitions



To understand what we have observed, we examine the contents of the container. We find that, at temperatures below 0 °C, the water in the container is now an equilibrium mixture of water vapor and solid water (ice), and there is no liquid present. The direct transition from solid to gas, without liquid, is called “sublimation.” For pressure-temperature combinations along this new curve below 0 °C, the curve shows the solid-gas equilibrium conditions. As with the liquid-vapor curve, we can interpret this new curve in two ways. The solid-gas curve gives the vapor pressure of

the solid water as a function of temperature, and also gives the sublimation temperature as a function of applied pressure.

Figure 2 is still not a complete phase diagram, because we have not included the combinations of temperature and pressure at which solid and liquid are at equilibrium. As a starting point for these observations, we look more carefully at the conditions near 0 °C. Very careful measurements reveal that the solid-gas line and the liquid-gas line intersect in Figure 2 where the temperature is 0.01 °C. Under these conditions, we observe inside the container that solid, liquid, and gas are all at equilibrium inside the container. As such, this unique temperature-pressure combination is called the “triple point.” At this point, the liquid and the solid have the same vapor pressure, so all three phases can be at equilibrium. If we raise the applied pressure slightly above the triple point, the vapor must disappear. We can observe that, by only slightly varying the temperature, the solid and liquid remain in equilibrium. We can further observe that the temperature at which the solid and liquid are in equilibrium varies almost imperceptibly as we increase the pressure. If we include the solid-liquid equilibrium conditions on the previous phase diagram, we get Figure 3, where the solid-liquid line is very nearly vertical.

Figure 3
Phase Diagram of H₂O

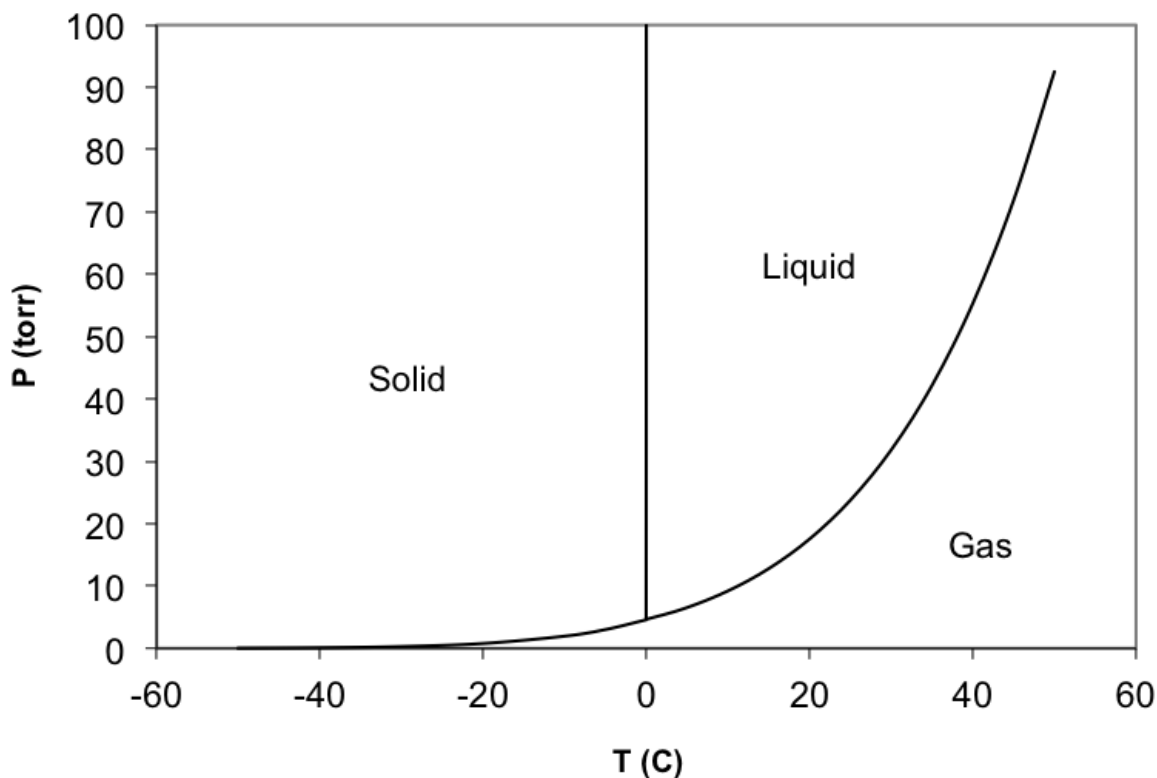


Figure 3 is an example of a complete phase diagram. This diagram shows for each temperature and pressure which phase or phases are present at equilibrium. Figure 3 is for water, but each substance has its own unique phase diagram, similar in appearance.

Observation 3: Boiling Points and Intermolecular Forces

Earlier in this study, we determined that the boiling point of a liquid is the temperature at which the vapor pressure of the liquid equals the pressure applied externally, e.g. by the atmosphere or by a piston trapping the liquid and gas in a cylinder. When the applied pressure is 1 atm, we refer to this as the “normal boiling point.” If we compare the normal boiling points of two liquids, the liquid with the higher normal boiling point clearly requires a

higher temperature to reach a vapor pressure of 1 atm. From our work on dynamic equilibrium, we know that this higher temperature is required to provide sufficient kinetic energy for the molecules in the liquid to overcome stronger attractions between the molecules. Overcoming these attractions is necessary for a molecule to “escape” the liquid and join the vapor phase.

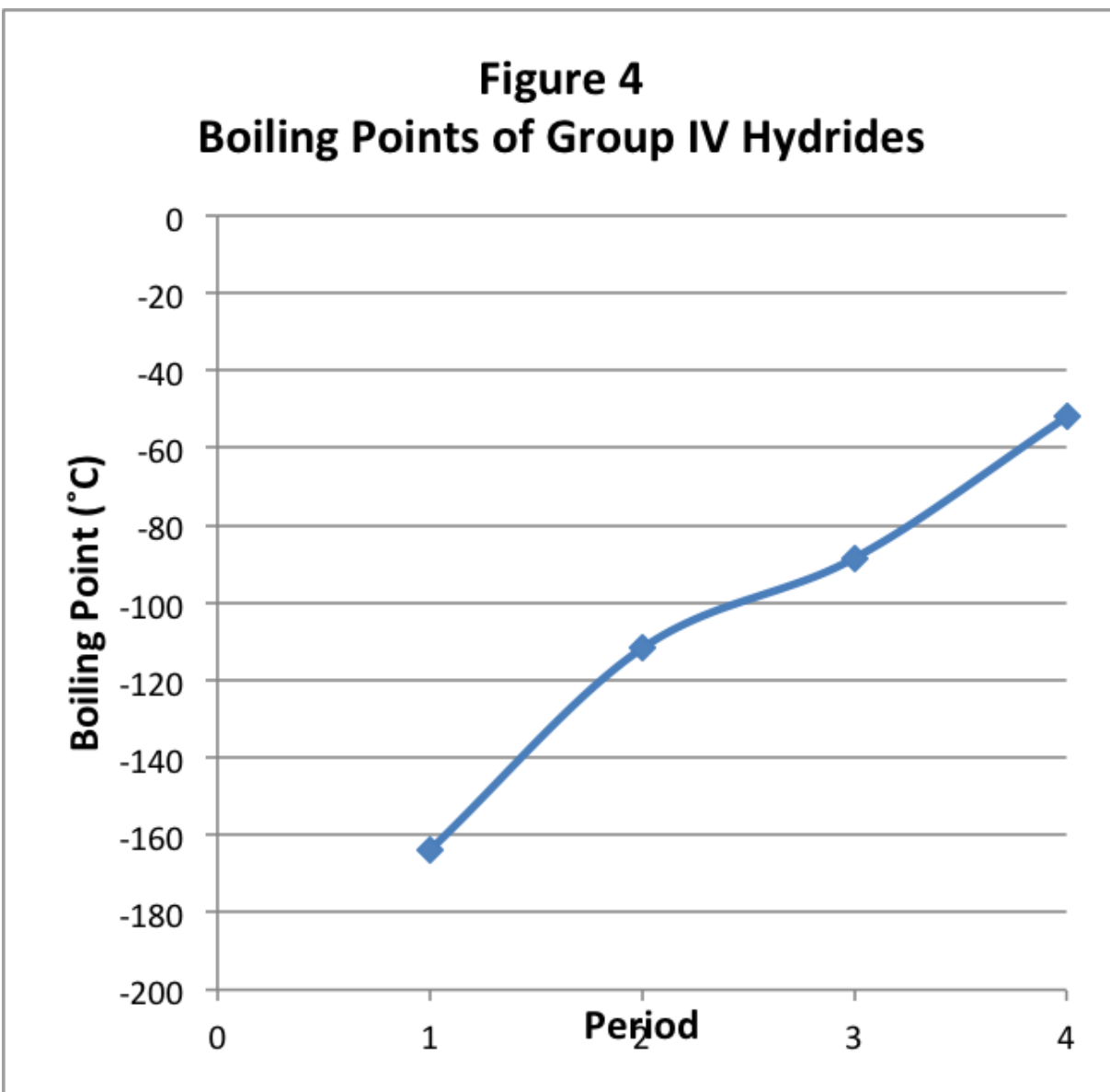
This line of reasoning means that, when we compare the normal boiling points of two liquids, we are also indirectly comparing the strengths of the intermolecular attractions in those two liquids. The liquid with a higher boiling point has stronger intermolecular attractions.

What determines the strength of these attractions? To find out, we can analyze experimental data for the boiling points of many liquids and look at the properties of the corresponding molecules. A useful set of compounds to look at are the covalent compounds formed by combining hydrogen with each of the elements in the “main group,” Groups IV to VII. For example, in the first row of the periodic table, these include CH₄, NH₃, H₂O, and HF. Table 1 gives the experimentally observed normal boiling points of the sixteen hydrides from Groups IV to VII in the first four rows of the periodic table.

	Boiling Point (°C)
CH ₄	-164
NH ₃	-33
H ₂ O	100
HF	20
SiH ₄	-111.8

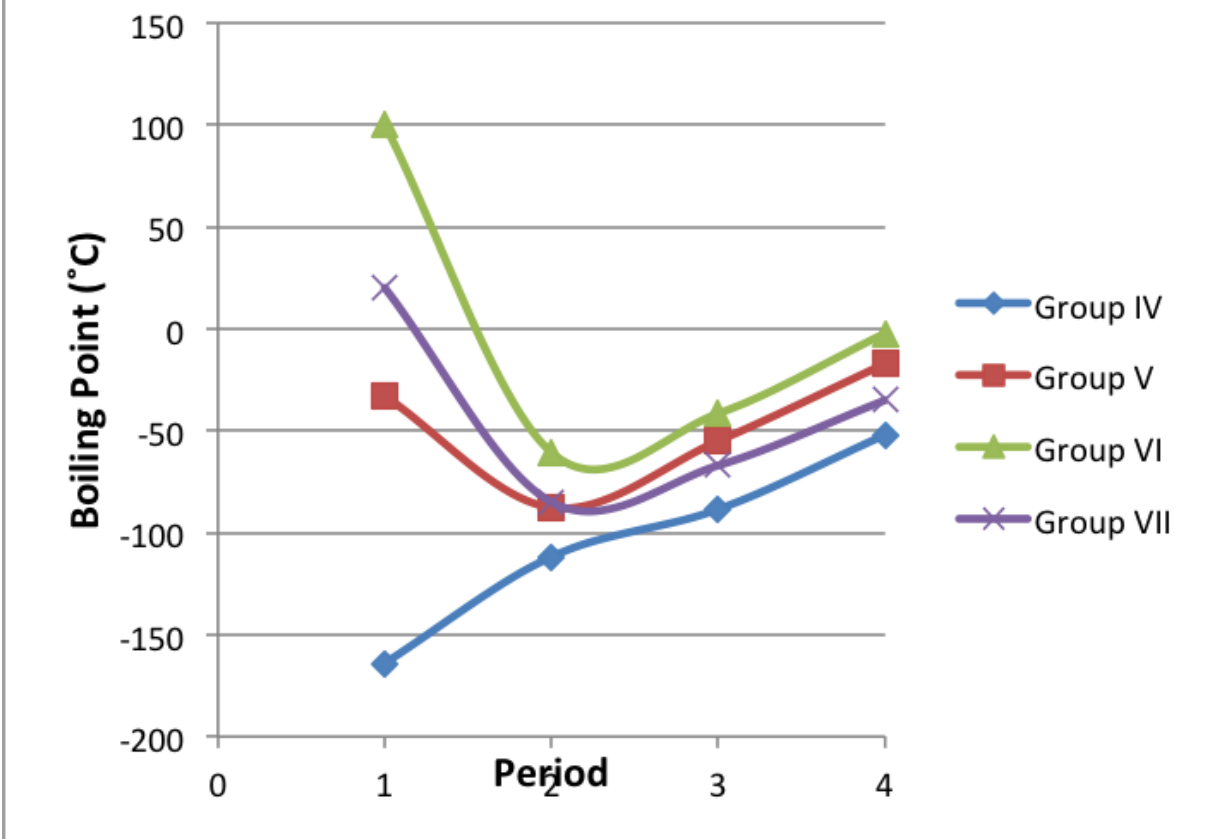
PH ₃	-87.7
H ₂ S	-60.7
HCl	-85
GeH ₄	-88.5
AsH ₃	-55
H ₂ Se	-41.5
HBr	-67
SnH ₄	-52
SbH ₃	-17.1
H ₂ Te	-2.2
HI	-35

At first glance, the values of the boiling points seem to be all over the place. Any patterns that might exist are not obvious. But there are patterns if we look at the data long enough, and those patterns can reveal to us what determines the intermolecular attractions. First, we can see that, for the compounds in each row of the periodic table, the compound with the lowest boiling point is from Group IV: CH₄, SiH₄, GeH₄, and SnH₄. Note that these are not the lowest four boiling points in Table 1. Rather, for each period, they are lowest boiling points of the compounds in each period. Notice also that the boiling points increase as we move down the table in Group IV, so that the heavier mass molecules have higher boiling points. This is easiest to see if we put them together on a chart in Figure 4.



These two observations suggest that we might find patterns if we put all of the sixteen hydrides on a chart together, sorted by the period each are in. The result is shown in Figure 5, which is just Figure 4 expanded to show all four groups in the data set of Table 1. With this chart, we see that the two patterns we described for Group IV work for Groups V to VII, but we also see three dramatic exceptions to those patterns in H_2O , NH_3 , and HF .

Figure 5
Boiling Points of Hydrides

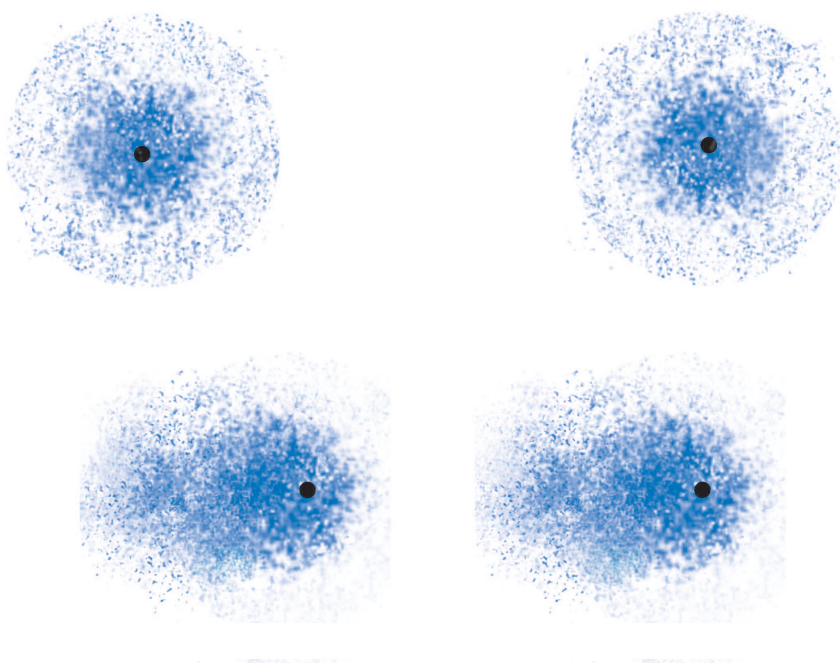


First, as we noted before, the hydrides from Group IV are the lowest boiling point compounds in each period. Second, in each group, the boiling point increases as we move down the periodic table. In fact, this second pattern is perhaps the most pronounced trend in the data. From this, we draw our first conclusion about the strengths of intermolecular attractions: for similar types of molecules, the molecules with larger atoms (more mass, more protons) have stronger intermolecular attractions.

Why would this be? The answer is not obvious but does make sense once we know it. Remember that these are all neutral molecules. As such, we might have imagined that there would be no positive-negative interactions. However, each molecule consists of a large number of protons from the nuclei of the atoms, and an equal number of electrons, both core electrons and valence electrons, which are either shared or unshared. When two

molecules are close to each other, the positive and negative charges in each of the molecules interact with each other. We might again imagine that the attractions of opposite charges would be exactly offset by the repulsions of like charges. This would be true if the charges were uniformly distributed in the molecules, as we would expect for non-polar molecules. But when the molecules are close enough to each other, the attractions and repulsions cause the charges to rearrange such that the attractions become significantly more favorable.

Such an arrangement of electrons in two adjacent highly simplified molecules is shown in Figure 6. Note that two nonpolar molecules become polarized when they are close to each other, due to the attraction of the negative charges in one molecule to the positive charges in the other molecule, and vice versa. The result is a net attractive force between the two molecules. This type of force is called the “dispersion force,” sometimes also called the “London force” after the discoverer.



What makes the dispersion force larger? The data in Table 1 and Figure 5 tell us: molecules with more positive and negative charges, like SnH_4 , have stronger attractions than molecules with fewer positive and negative

charges, like CH_4 . We say that the molecule with more charges is more “polarizable,” meaning it is easier for the molecule to become polarized in the presence of other electrical charges. The more polarizable a molecule is, the stronger the intermolecular forces will be.

Let’s now compare the boiling points of compounds in the same period from Group IV and from Group VII, e.g. SiH_4 versus HCl . The boiling point of HCl is larger. However, if we count the charges in these two molecules, we discover that they have the same number of electrons and the same number of protons. This suggests that the two molecules should be equally polarizable and therefore should have equal dispersion forces and therefore should have equal boiling points. But this is not true. Something else must be contributing to the difference in boiling points than just the dispersion forces.

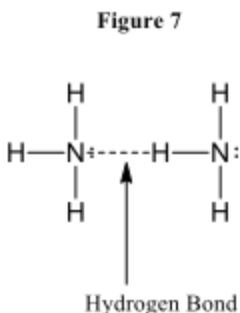
To spot the difference between these two molecules, we need to rely on our previously developed knowledge of electronegativities, molecular geometries, and molecular polarity. HCl is a polar linear molecular because the Cl atom is much more electronegative than the H atom. Si atoms are actually slightly less electronegative than H atoms, suggesting that SiH_4 should also be polar. But, we also recall from our electron domain model that SiH_4 has a symmetric tetrahedral geometry, like CH_4 . As such, like CH_4 , SiH_4 has no molecular dipole moment. From this comparison, we can conclude that, in comparing two molecules with similar dispersion forces, the molecule with a dipole moment will have stronger intermolecular attractions than the molecule without a dipole moment. This explains why, in each period in Figure 5, the Group IV hydride compound always has the lowest boiling point. Each of these compounds has nonpolar molecules due to their symmetry. By contrast, two HCl molecules will have stronger attractions as the positive end of one HCl will be attracted to the negative end of the other HCl , and vice versa.

We can now conclude that molecules attract one another via dispersion forces and, if the molecules are polar, via dipole-dipole attractions. Understanding these two types of intermolecular attractions works well to explain the major patterns observed in Figure 5.

This does not explain the exceptions, however. Why are the boiling points of NH_3 , H_2O , and HF so abnormally high? Given that these are small mass molecules, we would not expect them to have larger than average dispersion forces. All three are polar molecules, but there is nothing to suggest that their dipole moments are unusually high. There must be a different type of intermolecular attraction that is unique to these three molecules out of this set of molecules.

We need a pattern to analyze. What do these three molecules have in common with each other that the other molecules in Table 1 do not? N, O, and F are all strongly electronegative atoms and are also amongst the smallest atoms in the periodic table. In the Lewis structures for all three molecules, O, N and F all have non-bonded, lone pairs of electrons. These three properties, taken together in a single molecule, must present a uniquely strong intermolecular attraction.

Chemists account for this strong bonding via a model called “hydrogen bonding.” This is a uniquely strong form of dipole-dipole attraction that only occurs when a molecule contains a hydrogen atom bonded to an N atom, an O atom, or an F atom. Due to the strength of the electronegativity of these atoms, the N-H bond or O-H bond or F-H bond is highly polar, meaning that the H atom is almost a bare, positively charged hydrogen nucleus. This strong positive charge on one molecule is in turn strongly attracted to the negatively charged lone pair electrons on the N, O, or F atom of another molecule. This is illustrated in Figure 7.



Note that size seems to be important in hydrogen bonding as well. HF has a much higher boiling point than HCl , indicating that HF has stronger

intermolecular attractions. Even though the Cl atom is strongly electronegative and has lone pair electrons in the HCl molecule, the Cl atom is apparently too large to support the uniquely strong dipole-dipole attraction we call hydrogen bonding.

It turns out that other measurements and calculations reveal that, when present, hydrogen bonding attractions are approximately ten times stronger than dipole-dipole attractions or dispersion forces, for comparably sized molecules. Thus, hydrogen bonding dominates intermolecular attractions for those molecules which are capable of hydrogen bonding.

Of course, these conclusions are based on the set of data in Table 1 and Figure 5. These sixteen molecules are all somewhat comparable, consisting of no more than 5 atoms, and no more than one atom other than hydrogen. The boiling points of other molecules can reveal other trends in the strengths of intermolecular attractions. We will take one example to illustrate this. Let's compare the normal boiling point of H_2O , 100°C , to that of octane (C_8H_{18}), which is 125°C . Octane is symmetric, has no dipole moment, and has no N, O, or F atoms that could hydrogen bond. Therefore, octane molecules attract each other entirely through dispersion forces. And yet, the strength of the attractions between octane molecules is greater than that between water molecules. This reveals that the magnitude of the dispersion force can be dominant in comparing molecules of very different sizes. Dispersion forces can dominate both dipole-dipole interactions in polar molecules, and even hydrogen bonding forces.

Therefore, in attempting to predict which of two molecules might have the stronger intermolecular forces, it is important first to consider first whether the molecules are of comparable sizes or of very different sizes. Provided that the molecules are of comparable size, the dispersion forces should not be too very different. In this case, polar molecules will have stronger intermolecular forces than non-polar molecules, and molecules which exhibit hydrogen bonding will have even stronger intermolecular forces.

Review and Discussion Questions

1. In the phase diagram for water in Figure 1, start at the point where $T = 60\text{ }^{\circ}\text{C}$ and $P = 400\text{ torr}$. Slowly increase the temperature with constant pressure until $T = 100\text{ }^{\circ}\text{C}$. State what happens physically to the water during this heating process.
2. In the phase diagram for water in Figure 1, start at the point where $T = 60\text{ }^{\circ}\text{C}$ and $P = 400\text{ torr}$. Slowly lower the pressure at constant temperature until $P = 80\text{ torr}$. State what happens physically to the water during this process.
3. Explain why Figure 1 is both a graph of the boiling point of liquid water as a function of applied pressure and a graph of the vapor pressure of liquid water as a function of temperature.
4. Using arguments from the Kinetic Molecular Theory and the concept of dynamic equilibrium, explain why, at a given applied pressure, there can be one and only one temperature, the boiling point, at which a specific liquid and its vapor can be in equilibrium.
5. Using dynamic equilibrium arguments, explain why a substance with weaker intermolecular forces has a greater vapor pressure than one with stronger intermolecular forces.
6. The vapor pressure of phenol is 400 torr at about $160\text{ }^{\circ}\text{C}$, whereas the vapor pressure of dimethyl ether is 400 torr at about $-40\text{ }^{\circ}\text{C}$. Which of these substances has the greater intermolecular attractions? Which substance has the higher boiling point? Explain the difference in the intermolecular attractions in terms of molecular structure.
7. In Table 4 and Figure 5, the boiling point of stannane (SnH_4) is $-52\text{ }^{\circ}\text{C}$ and the boiling point of phosphine (PH_3) is $-87.7\text{ }^{\circ}\text{C}$. SnH_4 is non-polar and PH_3 is polar. Explain why the boiling point of SnH_4 is nevertheless higher than the boiling point of PH_3 .
8. Figure 5 shows that the boiling points of the hydrides in the first period are all unexpectedly high, except for methane (CH_4). Explain why CH_4 is an exception to this trend.

Phase Equilibrium in Solutions

Introduction

In our study of phase equilibrium, we have examined only pure materials. However, we will eventually want to study chemical reactions, which will mean understanding solutions with many components that might react with one another. Before considering reactions then, we need to consider what happens to phase equilibrium when there is more than one component present. How does mixing things together change equilibrium? This is actually a quite general question that we will address in many contexts including chemical reactions. For now, we'll consider the phase equilibrium first, since that is where we have discovered equilibrium and that is where we have developed an understanding based on the concept of dynamic equilibrium.

There are many types of solutions to consider. We can mix together gases with gases, liquids with liquids, gases with liquids, solids with liquids, and so on. Each of these present different challenges, but we will find that there are similarities amongst them as well. In particular, we'll find that dynamic equilibrium can be applied in each of these cases to understand the phase equilibrium that exists amongst the different components of the solutions.

Foundation

We will assume some understanding of solutions. Recall that the solvent is the major component in a solution, and is typically but not always a liquid. Far more often than not in Chemistry we use water as our solvent. A solute is a minor component of a solution, and in a single solution there may be more than one solute. The solute, in its pure form, can be a solid, another liquid, or even a gas. Once in solution, the solute usually has very different properties and is generally no longer recognizable from its pure form. Think about dissolving sugar or salt in water. The solution formed shows no evidence of the original crystalline solid solute.

Solutions are defined in large part by the concentration of the solute in the solvent. There are many ways to define and measure the concentration. The

most common is the “molarity” of the solution, meaning the number of moles of solute per liter of solution. The units of molarity are “molar” with a capital M: a solution with 1.0 mole of solute in 1.0 L of solution is a 1.0 M solution. In this study we will also discuss the mole fraction of the solute. This is simply the number of moles of solute divided by the total number of moles of particles of all types in the solution.

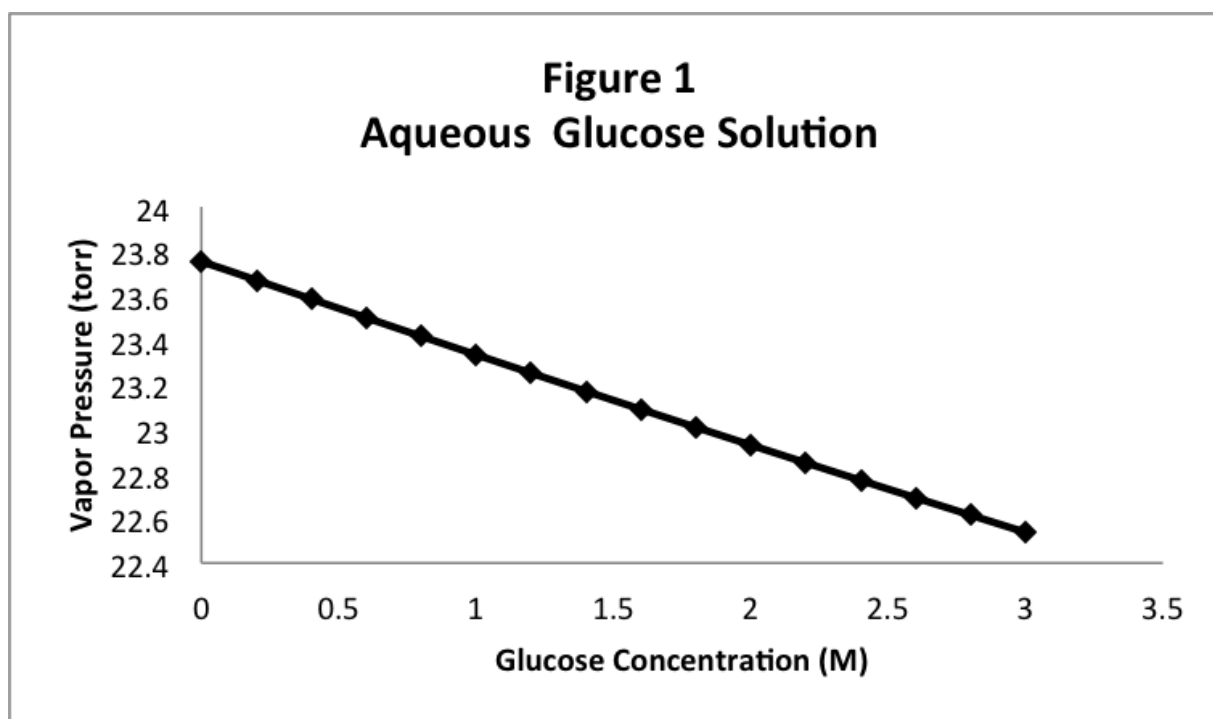
We will lean very heavily on the concept of dynamic equilibrium. The idea will show up in all of our explanations that two competing processes at equilibrium must have the same rate. We will examine several types of processes and the factors that determine their rates.

Observation 1: Lowering of the Vapor Pressure in Solution

To begin studying solutions, our first task is to observe what impact, if any, the presence of a solute has on the properties of the solvent. We will begin with a simple two-component solution, with a solvent and a single solute. The type of solute will matter to us, as we will observe different behaviors for different solutes, particularly whether the solute is, in its pure form, a solid, a liquid, or a gas. To start, we will consider solutions formed by dissolving a solid solute into a liquid solvent. This choice is easiest to start with because the solid solute will be assumed to be non-volatile. That is, it does not readily evaporate and therefore has zero vapor pressure. Solids do have a vapor pressure, but for most solids, the vapor pressures are sufficiently small that we can ignore them. As a first guess, then, we might assume that the solution formed from a volatile solvent and a non-volatile solute would have the same vapor pressure as the solvent alone, since the solute seems to contribute nothing to the equilibrium vapor pressure.

To study this question, we return to our familiar apparatus for studying vapor pressure. Consider trapping a quantity of liquid in a cylinder with a piston, which is then pulled back to create a volume above the liquid. We then measure the pressure in that volume, which is the pressure created by the vapor in equilibrium with the liquid. Recall that the pressure we observe is independent of the volume of liquid we trap, so long as there is some liquid remaining in the cylinder, or as long as the liquid does not all evaporate.

In this case, instead of trapping pure water in the cylinder, we will trap a solution of glucose in water. Just to be quantitative, we'll make this a 1.0 M solution of glucose. Recall that the vapor pressure of pure water at 25 °C is 23.756 torr. When we measure the vapor pressure of the glucose solution, we find a different value, 23.33 torr, lower than the vapor pressure of the pure water. To check this, we measure the vapor pressure of a 2.0 M glucose solution, and we observe 22.93 torr. Note that the higher concentration has an even lower vapor pressure. If we look at these numbers carefully, we notice that the amount by which the vapor pressure was lowered for the 2.0 M solution (0.82 torr) seems to be about double the lowering for the 1.0 M solution (0.42 torr). To verify this trend, we can try several solutions and plot the vapor pressure as a function of the concentration of the glucose solution. The result is shown in Figure 1, where the vapor pressure appears to decrease in a linear fashion as we increase the concentration of glucose.

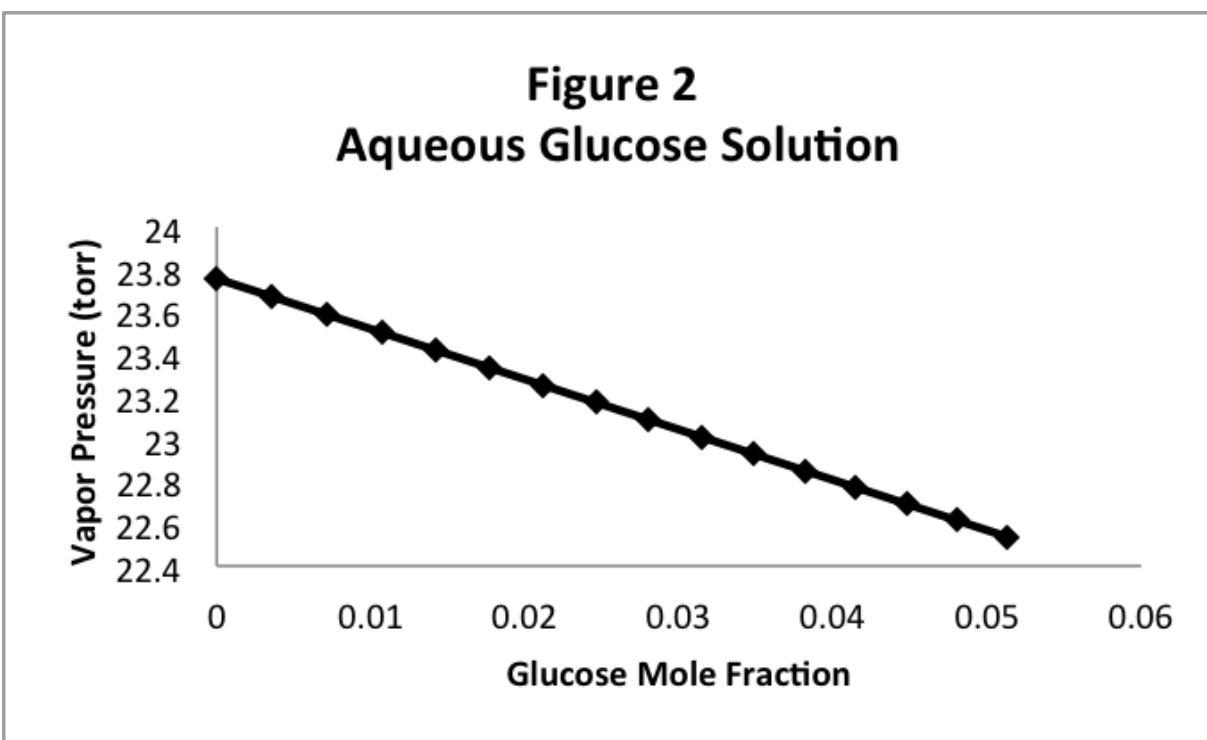


It isn't obvious just from looking, but the graph in Figure 1 is not exactly a straight line. It curves slightly. It isn't obvious either that we can get a better straight line by changing the way in which the concentration of the glucose

is measured. Instead of using the molarity (moles per liter), we can measure the “mole fraction” of the glucose, defined by:

$$X_{\text{glucose}} = n_{\text{glucose}} / (n_{\text{glucose}} + n_{\text{water}})$$

Note that the mole fraction is, as the name suggests, the fraction of the total number of moles of substance that is glucose. If we plot the vapor pressure of the glucose solutions as a function of the mole fraction of glucose, we get the graph in Figure 2, which essentially turns out to be a perfectly straight line.



Based on the graph in Figure 2, we can say that the vapor pressure of the glucose solution is a linear function of the mole fraction of the glucose in the solution. With a little work, we can show that the line in Figure 2 is described by the equation:

$$P_{\text{vap}} = P_{\text{vap}}^* (1 - X_{\text{glucose}})$$

where P_{vap}^* is the vapor pressure of the pure water. This means that it is only the number of moles of glucose that affects the vapor pressure of the solution. If we look back at the definition of mole fraction, we can see that the mole fraction of glucose plus the mole fraction of water must equal 1. This means that $X_{\text{glucose}} + X_{\text{water}} = 1$, so we can rewrite the above equation as:

$$P_{\text{vap}} = P_{\text{vap}}^* X_{\text{water}}$$

This is a somewhat unexpected result: glucose seems to be absent from the equation! In fact, it is present, but only in the expression for the mole fraction of water

We should check this result by comparing it to other aqueous solutions of nonvolatile solutes. Ethylene glycol, commonly used in antifreeze solutions, is soluble in water but has a very small vapor pressure at 25 °C, less than 0.1 torr. When we prepare ethylene glycol solutions with molarities in the range of 1.0 M to 3.0 M and measure the vapor pressures as before, we discover a remarkable result. The vapor pressures follow the same graphs as shown in Figures 1 and 2. There is no discernible difference within the accuracy of our measurements. This means that, in our equation $P_{\text{vap}} = P_{\text{vap}}^* X_{\text{water}}$, the vapor pressure of the aqueous solution does not depend on the identity of the nonvolatile solute. It depends only on the number of moles of the nonvolatile solute. This is not at all an intuitive result. However, it is quite general, and these experimental results and the equation above both go by the name “Raoult’s Law.” Raoult’s measurements showed that this equation works for almost all solvent and nonvolatile solute combinations, provided only that the concentration of the solute is not too high.

Given this surprising result, we need to generate a model which can account for it. Before doing so, we will consider an additional aspect of our observation. Imagine that we start with pure liquid water in equilibrium with its vapor at the normal boiling point. This means that the temperature is 100 °C, and the applied pressure and the vapor pressure are both 1 atm. Now imagine that we add some amount of glucose to the water. According to Raoult’s law, the vapor pressure of the solution we just formed must be less than the vapor pressure of the pure water. Therefore, the vapor pressure

is less than 1 atm, which is less than the applied pressure. Since the applied pressure is greater, all of the vapor must now condense into the liquid, and we no longer have liquid-vapor equilibrium. The solution is not at its boiling point, even though the temperature is 100 °C. The addition of the nonvolatile solute has disrupted the liquid-vapor equilibrium.

How can we restore the equilibrium? There are two ways. The obvious way would be to lower the applied pressure to the vapor pressure of the solution. A less obvious way would be to increase the temperature without changing the applied pressure. To see this, remember that Raoult's law gives the vapor pressure of the solution in terms of the vapor pressure of the pure liquid: $P_{\text{vap}} = P_{\text{vap}}^* \cdot X_{\text{water}}$. If we need P_{vap} to be 1 atm even though X_{water} is less than 1, we can increase P_{vap}^* by increasing the temperature. This means that we can find a normal boiling point for the solution, but it will be at a higher temperature than the boiling point of the pure liquid at the same applied pressure. The boiling point is *elevated* by the presence of the nonvolatile solute. The amount by which the boiling point changes is typically quite small, about 0.5 °C for a 1 M solution, but it is easily observable.

Dynamic Equilibrium and Vapor Pressure Lowering

There are really two interesting observations in Raoult's law. One is that the vapor pressure is lowered when a nonvolatile solute is dissolved in a volatile solvent. The other is that the amount of that lowering does not depend on what the nonvolatile solute is. It depends only on the mole fraction of the nonvolatile solute in the solution. We need to develop a model which accounts for both of these observations.

Our starting point will be the dynamic equilibrium model we developed in the previous Concept Development Studies. Remember the essential point of this model: at liquid-vapor equilibrium, the rate of evaporation of the liquid is exactly equal to the rate of the condensation of the vapor. As we have just observed, the presence of a solute disrupts this equilibrium: adding a nonvolatile solute to a boiling solvent stops the boiling until the temperature is raised. Our question is then, which of the processes was disrupted: condensation, evaporation, or both?

Let's start with condensation of the vapor. Remember that the solute is nonvolatile, which means that there are no solute molecules in the vapor phase. This indicates that the rate of condensation depends only on the number of moles per volume of solvent molecules in the vapor phase. When we add solute to the liquid phase solution, that number does not change. So the rate of condensation is the same, whether the solute is present or not, when the pressure of the vapor is the same.

This means that it is the rate of evaporation that must be disrupted by the presence of the solute. That does make sense, since we added the solute only to the liquid phase and evaporation is the process by which molecules leave the liquid phase and enter the vapor phase. Furthermore, after adding the solute, we observed that a new equilibrium is established at a lower vapor pressure. This means that at equilibrium the rate of condensation is lower than it was before we added the solute. So, at equilibrium, the rate of evaporation must be lower once we add the solute.

We can conclude that the rate of evaporation is lowered by the presence of a nonvolatile solute. This means that, for dynamic equilibrium, the rate of condensation must also be lower, which means that the pressure of the vapor must be lower at equilibrium.

What remains is to work out why the rate of evaporation is lowered by the solute. Here it is helpful to remember the second observation of Raoult's law, which concludes that the amount of the vapor pressure lowering depends only on what fraction of the moles of particles present in the solution are solute particles. This is an important clue. Evaporation requires that solvent molecules overcome intermolecular attractions and "escape" the liquid phase. Not every solvent molecule is well positioned for an escape, regardless of whether it has sufficient kinetic energy. A solvent molecule must be near the surface of the liquid if it is to escape unfettered by running into other solvent molecules that will slow it down. Since the rate of evaporation is lower when the solute is present, the solute particles must reduce the number of solvent molecules which are positioned and available for evaporation near the surface of the liquid. The solute molecules impair the ability of solvent molecules to escape. And they do so in ways which do not depend on what the solute molecules are.

Why would the solute molecules impair the escape of the solvent molecules into the vapor? There are two ways to think about this, one more complicated than the other. A simple picture would be that, on and near the surface of the liquid, some of the surface area of the solution is occupied by the solute particles. The fraction of that surface taken up by solute molecules could be assumed to be the same proportion as the fraction of solute molecules in the solution. This would immediately account for Raoult's law: solute molecules near the surface reduce the rate of evaporation in proportion to their mole fraction by taking up space near the surface. To match this lower rate of evaporation, the vapor pressure must be lower so that the rate of condensation is lower to achieve equilibrium.

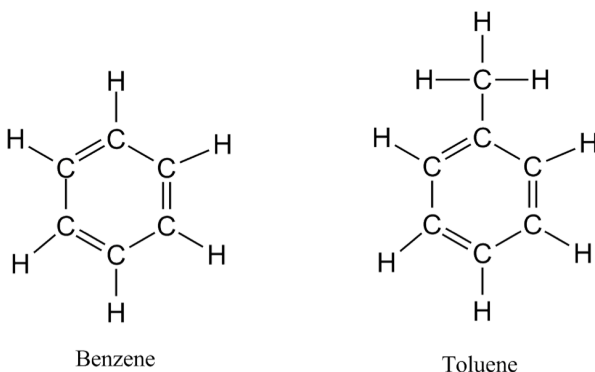
This is a nicely intuitive model, but it is somewhat inaccurate. In solution, solute molecules are surrounded by solvent molecules, a process called "solvation." This is actually why a nonvolatile solute dissolves. This solvation process ties up solvent molecules, reducing their ability to escape from the solution, and it does so in proportion to the fraction of solute molecules in the solution. The effect is exactly the same as described in the simpler model described above, but it is worth keeping in mind that solute molecules are always solvated by solvent molecules. It is an important part of the process of forming a solution.

Let's conclude by applying our dynamic equilibrium argument to the elevation of the boiling point by the addition of a solute. The rate of condensation is determined by the pressure of the vapor, and for normal boiling to occur, that pressure must equal 1 atm. If the rate of evaporation is lowered by the presence of the solute, then that lowering must be overcome for the rate of evaporation to match the rate of condensation at 1 atm. The straightforward way to do this is to raise the temperature, thereby increasing the fraction of solvent molecules in the liquid with sufficient kinetic energy to escape the liquid. By elevating the temperature, we can restore the dynamic equilibrium, and this is why the boiling point must be elevated by the presence of solute molecules in the liquid phase.

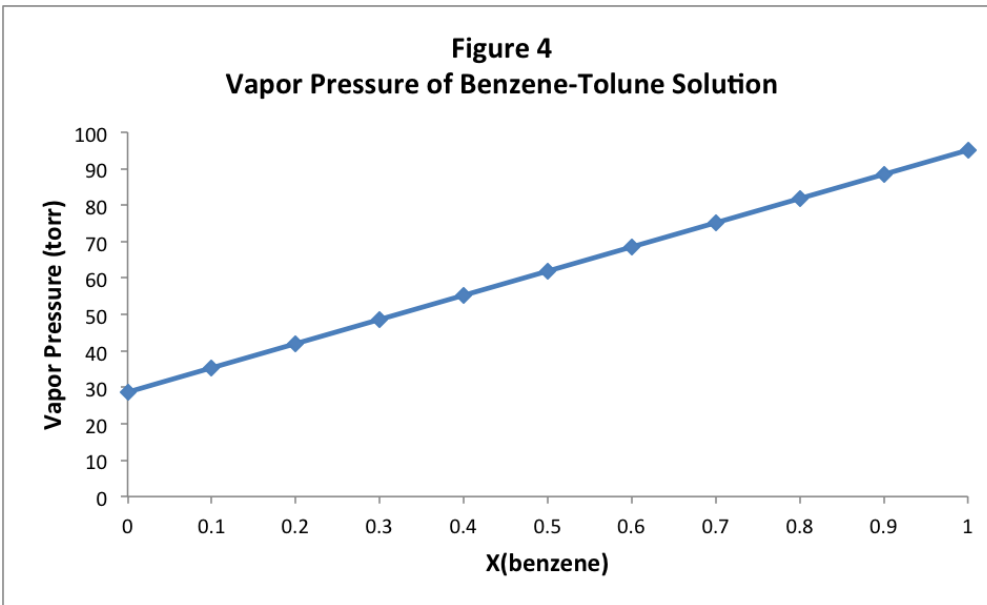
Observation 2: Vapor Pressures of Solutions with Two Volatile Components

So far, we have considered only solutions with a single volatile component, the solvent. In most cases, this means dissolving a solid into a liquid, but it can also mean dissolving a liquid with a very low vapor pressure into another liquid. There are other types of solutions, of course. For example, we can mix together two volatile liquids, dissolving each in the other to form a solution. Note that not all liquids are “miscible,” meaning that it is not always possible to form a liquid-liquid solution. For example, we have all observed that oil and water separate when mixed together and thus do not form a solution. In general, two liquids will tend to dissolve in each other when the intermolecular forces between the two types of molecules are similar. A good example is mixing water with ethanol. In each substance, the molecules attract each other with hydrogen bonding, so therefore the water and ethanol molecules will also attract each other with hydrogen bonding when combined in a solution.

A very good example of such mixing is for benzene and toluene, whose molecules are quite similar as shown in Figure 3:



Because of these similarities, benzene and toluene can be mixed in any proportion. Both of these liquids have significant vapor pressures. At 25 °C, the vapor pressure of benzene is 95.1 torr and the vapor pressure of toluene is 28.7 torr. What would we observe the vapor pressure to be if we were to take a solution of benzene and toluene? The experimental data are shown in Figure 4 at 25 °C.



We get a very simple linear relationship, increasing from the vapor pressure of pure toluene, when the mole fraction of benzene is 0, to the vapor pressure of pure benzene, when the mole fraction of benzene is 1. The equation for this straight line can be found simply to be:

$$P_{vap} = P^*_{toluene} + (P^*_{benzene} - P^*_{toluene})X_{benzene}$$

Where P_{vap} is the observed vapor pressure above the solution, and P^* is the vapor pressure of either pure toluene or pure benzene. We can slightly rearrange this equation by separating the benzene terms from the toluene terms and using the fact that $X_{benzene} = 1 - X^*_{toluene}$:

$$P_{vap} = P^*_{toluene} + P^*_{benzene}X_{benzene} - P^*_{toluene}X_{benzene}$$

$$P_{vap} = P^*_{toluene} + P^*_{benzene}X_{benzene} - P^*_{toluene}(1 - X_{toluene})$$

$$P_{vap} = P^*_{benzene}X_{benzene} + P^*_{toluene}X_{toluene}$$

Recall Raoult's law from earlier in this study, which generally states that $P_{vap} = P^*_{vap} \cdot X_{solvent}$. Both terms in the last equation above look just like Raoult's law for each component. This means that each component is contributing to the total vapor pressure of the solution exactly by what we would have expected it to contribute if it were the only volatile component of the solution. And the two vapor pressures add together simply just as we

would have expected from Dalton's Law of Partial Pressures, which is a result of the Ideal Gas Law.

When two liquids mix in solution to combine their vapor pressures in this very simple way, we call the solution "ideal." Generally, we observe this ideal behavior when the two components of the solution have molecules that have similar intermolecular forces.

We can understand this experimental result by thinking about dynamic equilibrium. In order for the solution to be in equilibrium with the vapor, each component must be in dynamic equilibrium. Each component lowers the rate of evaporation of the other component in the same way that a nonvolatile solute lowers the rate of evaporation of the solvent. Therefore, each component has a lower number of molecules in the vapor phase to balance the dynamic equilibrium. And the two components' vapor pressures add together to form the total solution vapor pressure because, at these low pressure, the kinetic molecular theory accurately describes the gas phase, so the Ideal Gas Law and Dalton's Law apply.

Observation 3: Equilibrium between Solids and Liquid Solutions

So far, we have only examined liquid-vapor equilibrium and the effects on that equilibrium by the presence of a solute in the liquid phase. However, we can easily observe that a solute in the liquid solvent also disrupts the equilibrium between the liquid solvent and its solid phase. The most prevalent observation of this involves the freezing of salt water. It has long been common practice in cold climates on icy days to spread salt over ice covered streets and sidewalks. This serves to melt the ice, despite the fact that the temperature of the air is below 0 °C. The added salt disrupts the normal solid-liquid equilibrium, allowing the ice to melt at temperatures below 0 °C. This means that the presence of the salt in the water lowers the freezing point of the water. Experimentally, we find that the freezing point of water is lowered by over 20 °C for a saturated salt solution. The lowering of the freezing point is a much larger effect than the elevation of the boiling point.

We can measure the freezing point of solutions of various concentrations, and similar to the change in vapor pressure, the experimental data show that the lowering of the freezing point is proportional to the mole fraction of the solute in the liquid phase. This leads us to consider how the presence of the solute disrupts the dynamic equilibrium and produces the change in the freezing point.

To develop a model to understand this, we need another experimental observation. When frozen water is in equilibrium with a salt solution, the solid water is pure water, containing no salt. As you may have read, icebergs floating in the ocean are actually pure water, not frozen salt water. When the salt water from the ocean freezes, the salt remains behind in unfrozen water, producing ice which is pure water without any salt. You can run this experiment yourself by freezing a sample of salt water, removing the ice on the top, and then melting that ice. The water produced is pure, not a salt solution.

This observation raises two questions: why is the solid ice made only of pure water instead of a frozen salt solution? And how does this disrupt the dynamic equilibrium between the liquid and the solid? Let's focus first on developing a model that helps answer the second question. For a pure liquid in equilibrium with a pure solid, e.g. ice and water at 0 °C and 1 atm pressure, the rate of freezing and the rate of melting must be equal. The rate of melting depends on the fraction of the molecules in the solid that have sufficient energy to break free of the crystalline structure of the solid, which depends on the temperature. At higher temperatures, more molecules have sufficient energy, and the solid melts. This is why liquids exist at temperatures higher than temperatures where solids exist. The rate of freezing depends on how frequently molecules in the liquid collide with the surface of the solid and are deposited there, losing their energy to the surrounding liquid molecules. This depends on the temperature, but also depends weakly on the pressure applied to the liquid and solid equilibrium.

Consider now adding the solute to the liquid solvent. Since the solute does not enter the solid phase, the rate at which molecules can escape the solid and join the liquid phase does not depend on the presence of the solute. So, the rate of melting is unchanged by the presence of the solute. But we know

that the freezing point is lowered by the presence of the solute in the liquid phase. Since the dynamic equilibrium is disrupted by the solute, it must be true that the rate at which molecules enter the solid phase is changed by the presence of the solute. If we don't change the temperature, adding the solute to the solid-liquid equilibrium causes the solid to melt. So it must be true that, when the solute is present, the rate of melting at the freezing point is greater than the rate of freezing. This means that the rate of freezing of molecules onto the surface of the solid is reduced when the solute is present.

This sounds familiar. The rate of evaporation of molecules from the liquid phase is reduced when solute molecules are present, and now we see that the rate of freezing of molecules from the liquid phase is also reduced when solute molecules are present. Perhaps the reasons are similar. In the case of evaporation, solute molecules reduce the number of solvent molecules that are available to evaporate. In the case of freezing, solute molecules also reduce the number of solvent molecules that are available to deposit on the solid surface. This makes sense when we remember that the solute molecules cannot enter the solid phase. In essence, the solute molecules block sites on the solid surface where solvent molecules could otherwise deposit. With a lower rate of freezing than the rate of melting, the melting process wins and the solid melts.

How can we restore equilibrium? The answer is that we must lower the rate of melting. This requires that there be fewer molecules in the solid phase with sufficient energy to break free of the crystal structure. To accomplish this, the temperature must be lower. Therefore, for solid-liquid equilibrium to be restored, we have to lower the temperature, therefore lowering the freezing point.

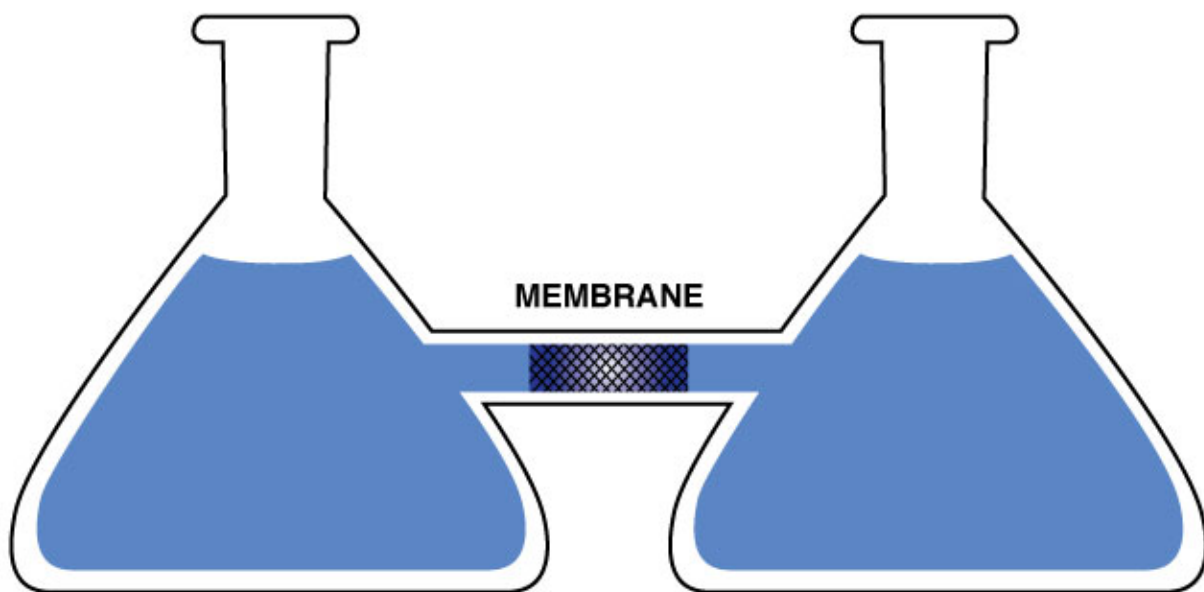
Observation 4: Equilibrium between a Solvent and a Solution

The last example we will consider is the least obvious but is also arguably the most significant for biological systems. In this case, we will observe a solvent in equilibrium with a solution containing that solvent. This sounds tricky: how can the solvent be separated from the solution so that they can

be in equilibrium with each other? Or, stated differently, how can there be two phases in such a case?

The experimental set-up may look somewhat contrived and artificial, but there are many systems in biology which have the same essential components. In Figure 5, we show flasks connected by a short glass tube. In the middle of the tube, there is a particular kind of membrane which is semi-permeable. A permeable membrane permits the passage of molecules back and forth through the membrane. A semi-permeable membrane will permit the passage only of smaller molecules; larger molecules are blocked from passing. Let's assume that our membrane will permit the passage of the solvent, which we'll take to be water, but will not permit the passage of a solute, which we'll take to be glucose. Now, let's fill both flasks up to their necks with water. Since the water can flow freely through the membrane, the level of water in both flasks will rise to the same level due to gravity. The two flasks are in equilibrium with each other, just as if the membrane wasn't there.

Figure 5



Now we will add glucose to the flask on the right. This would not seem to change anything because the glucose cannot cross the membrane from the right flask to the left flask. However, this is not what we observe

experimentally. Instead, we observe that the water level begins to rise in the flask on the right while the water level falls in the flask on the left. This means that the pure water in the left flask and the solution in the right flask are no longer in equilibrium with each other. This flow continues for a while but eventually stops, meaning that the flasks eventually come to equilibrium again, but with less water in the flask on the left than there is solution in the flask on the right.

The process by which a pure solvent passes through a semi-permeable membrane into a solution of the same solvent is called “osmosis.” Our task is to develop a model which accounts for osmosis. We once again turn to the concept of dynamic equilibrium.

Before the solute is added and the two flasks contain only pure water, the rate of flow of water from the left to the right must be exactly the same as the rate of flow of water from the right to the left. If this were not true, the water levels would be constantly changing. So, before adding the solute, we start with dynamic equilibrium. Adding the solute disrupts this equilibrium, since the water levels start to change once the solute is added. Since we only add the solute to the flask on the right, the solvent on the left is unchanged and the flow of water from left to right does not change. To account for the net flow of water from left to right, the flow of water from right to left must decrease when we add the solute. This once again sounds familiar. The presence of the solute must inhibit the flow of water through the membrane. Either the solute particles block some of the passages in the membrane, or some of the water molecules are bound up in solvating the solute particles and therefore cannot pass through the membrane. Viewed either way, the solute slows the flow of water from right to left, so there is a net flow of water from left to right. That is why we observe osmosis.

The left flask will always contain pure water in this set-up, since solute never travels from right to left. This would suggest that the osmosis should continue until there is no water remaining in the left flask. But that is not what we observe. Instead, after a while, the net flow stops and dynamic equilibrium is re-established. This is not expected. How can the rate of flow of water from right to left ever rise to meet the rate of flow of water from left to right? The clue to the answer is found by looking at the taller column

of water in the neck of the flask on the right. The water piling up in the column on the right generates an extra pressure on the water near the membrane, increasing the rate of flow from right to left. Once the pressure is high enough, the rate of flow from right to left matches the rate of flow from left to right and equilibrium is achieved. The pressure required to achieve equilibrium to counter osmosis is called the “osmotic pressure.” Experimental data show that the osmotic pressure, usually labeled as Π , is proportional to the molarity of the solute in the solution:

$$\Pi = MRT$$

Osmotic pressures can be quite high, several times more than the atmospheric pressure. This means that osmotic pressure can be a significant driving force in nature. For example, a biological cell wall is a semipermeable membrane, permitting the passage of water and some smaller molecules like O_2 or CO_2 , but not the passage of larger molecules like proteins. As a result, osmosis is the process by which the roots of plants extract water from the surrounding soil.

Review and Discussion Questions

1. The observed data in Figure 2 show us that the vapor pressure of the solution is proportional to the fraction of the molecules which are solvent molecules:

$$P_{\text{vap}} = P_{\text{vap}}^* \cdot X_{\text{water}}$$

Using dynamic equilibrium arguments, explain why the vapor pressure is proportional to the mole fraction of the solvent.

2. This same equation shows that the vapor pressure of the solution depends on the identity of the solvent, since P_{vap}^* depends on what the solvent is. But it does not depend on the identity of the solute. Using dynamic equilibrium arguments, explain both of these facts.
3. For a solution of two volatile liquids, Raoult's Law works very well in predicting the vapor pressure if the molecules of the two liquids are somewhat similar. For molecules which are quite different, Raoult's Law is not as accurate. Explain these observations using the dynamic equilibrium model.

4. The vapor above a solution of two volatile liquids is richer in the more volatile liquid than is the solution. Explain why this is true. Devise a way to use this observation to create a liquid solution which is significantly richer in the more volatile component than the original liquid solution.
5. In an old-fashioned homemade ice cream freezer, the ice cream mixture is placed in a container which is immersed in a slurry of ice and water. The slurry itself is contained in an insulated container. NaCl is usually added to the slurry. When the salt is added, the temperature of the slurry is observed to drop significantly by as much as 20 °C. Explain why the temperature drops when the salt is added. Hint: since temperature measures kinetic energy, the temperature drop signals a drop in kinetic energy. Think about where this energy goes.
6. To observe osmotic pressure, we must separate the solutions with a semi-permeable membrane. What would be observed if we were to replace the semi-permeable membrane with a permeable one? How would this affect the dynamic equilibrium?

Reaction Rate Laws

Introduction

We have observed competing processes in dynamic equilibrium in several different types of chemical processes. These include evaporation in dynamic liquid-vapor equilibrium with condensation. Similarly, we observed liquid-solid equilibrium, solutions in equilibrium, and solubility equilibrium involving both gases and ionic solids. It is clear from all of these studies that we need to understand the rates at which different processes occur, including what factors determine these rates. So far, these processes almost all involve pretty simple dynamics with fairly easy-to-understand rates. As we expand our studies into chemical reactions, however, we will encounter more complicated processes with more complicated rates of reaction.

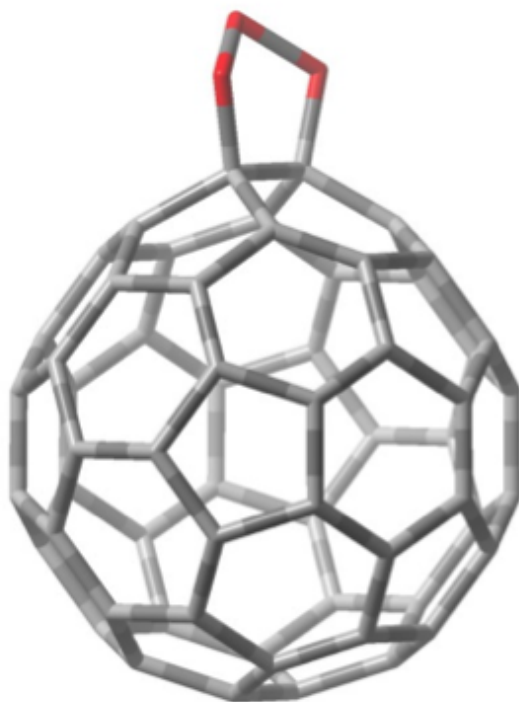
It is important to understand rates of chemical reactions for many reasons, only one of which is understanding equilibrium. In many cases, the speed of the reaction might be of more interest than the final equilibrium conditions of the reaction. Some reactions proceed so slowly towards equilibrium as to appear to not occur at all. For example, metallic iron will eventually oxidize in the presence of aqueous salt solutions, but the time it takes for this process to occur is sufficiently long that we can reasonably expect to build a boat out of iron. On the other hand, some reactions may be so rapid as to pose a hazard. For example, hydrogen gas will react with oxygen gas so rapidly as to cause an explosion. In addition, the time scale for a reaction can depend very strongly on the amounts of reactants and their temperature.

In this Concept Development Study, we seek an understanding of the rates of chemical reactions. We will define and measure reaction rates and develop a quantitative analysis of the dependence of the reaction rates on the conditions of the reaction, including reactant concentrations and temperature. In this study, we will restrict ourselves to this quantitative analysis of reaction rates. In the following study, we will use this insight to develop a model to provide an understanding of the significance of reactant concentration and temperature.

Foundation

In this study, we will assume very little prior knowledge, as we are beginning a new area of observation. We of course assume our understanding of the Atomic Molecular Theory, including the ideas of stoichiometry and balanced chemical equations. We will also assume an understanding of the postulates of the Kinetic Molecular Theory and of the energetics of chemical reactions.

Observation 1: Measuring the Rate of a Chemical Reaction



$C_{60}O_3$ is prepared from C_{60} dissolved in toluene solution at temperatures of 0 °C or below. When the solution is warmed, $C_{60}O_3$ decomposes, releasing O_2 and creating $C_{60}O$. This reaction goes essentially to completion, in other words all of the $C_{60}O_3$ decomposes creating an equal number of moles of $C_{60}O$. We can actually watch this process happen in time by measuring the amount of light of a specific frequency absorbed by the $C_{60}O_3$ molecules, called the “absorbance.” The absorbance is proportional to the concentration of the $C_{60}O_3$ in the toluene solution, so observing the absorbance as a function of time is essentially the same as observing the concentration as a function of time. One such set of data is given in Table 1, which is shown in the graph in Figure 2.

time (min)	$C_{60}O_3$ absorbance
3	0.04241
9	0.03634
15	0.03121
21	0.02680
27	0.02311
33	0.01992
39	0.01721
45	0.01484
51	0.01286

time (min)	C₆₀O₃ absorbance
57	0.01106
63	0.00955
69	0.00827
75	0.00710
81	0.00616
87	0.00534
93	0.00461
99	0.00395

C₆₀O₃ Absorbance during Thermal Decomposition at 23 °C

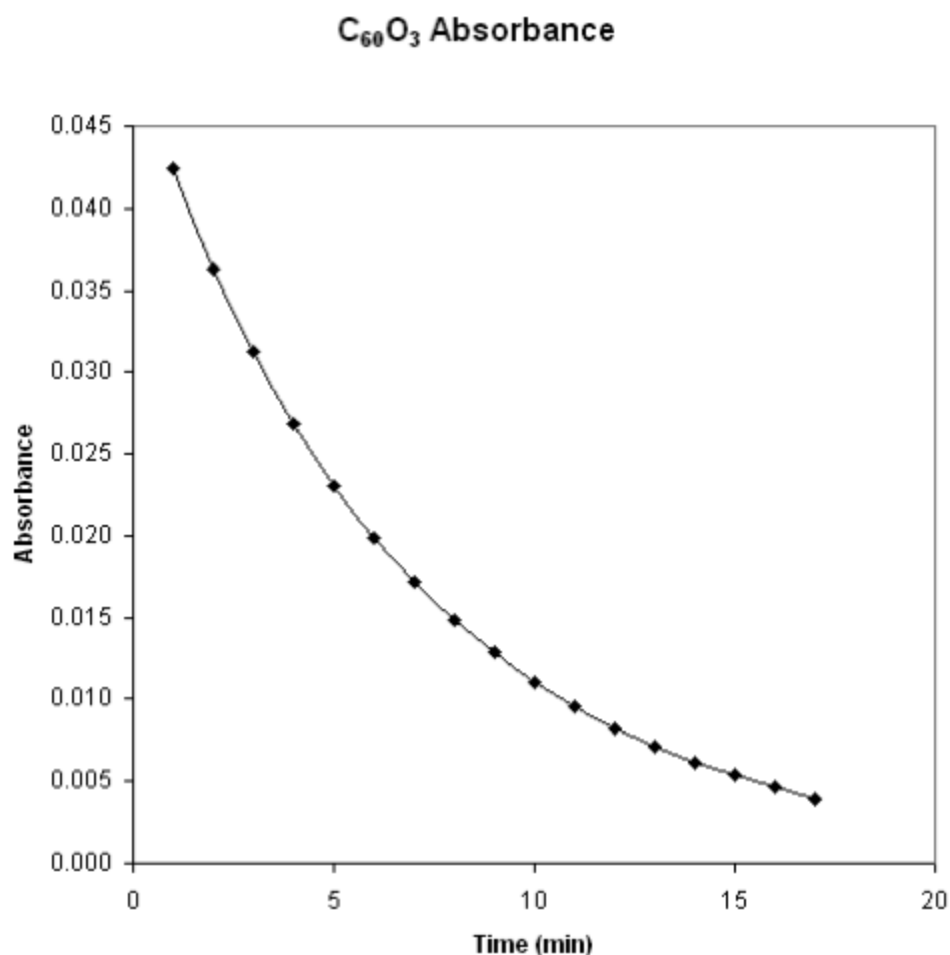


Figure 2

The rate of the decomposition reaction is the same as the rate of change in $[C_{60}O_3]$, since the reaction reduces this concentration. The rate of change in the concentration is proportional to the slope of the graph in Figure 2. Therefore, we define the rate of this reaction as

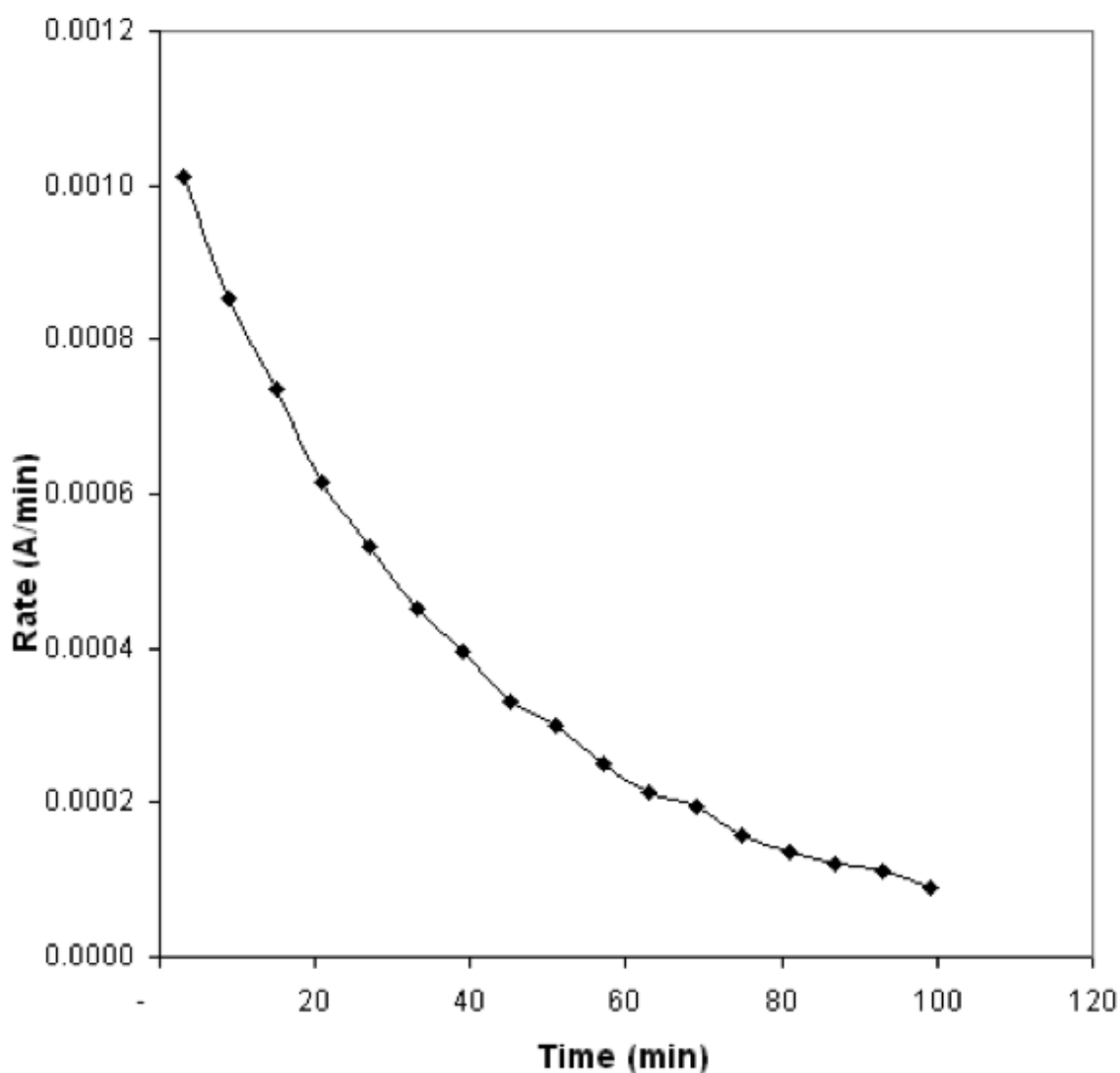
$$Rate = \frac{d[C_{60}O_3]}{dt} \approx - \frac{\Delta[C_{60}O_3]}{\Delta t}$$

Technically, we should take the derivative of the curve in Figure 2, since the graph is not a straight line, but we can make an excellent estimate by taking

differences as shown in this equation. Notice we have added a negative sign to the rate of change of the concentration. This is because we want the rate of reaction to be positive, since the reaction is proceeding forward.

However, we are measuring the rate of disappearance of the reactant in this case, which is a negative number. By including a negative sign in the definition of reaction rate in Equation (1), the rate is a positive number. The rate, calculated in this way, is plotted as a function of time in Figure 3.

Figure 3
Rate of Decomposition

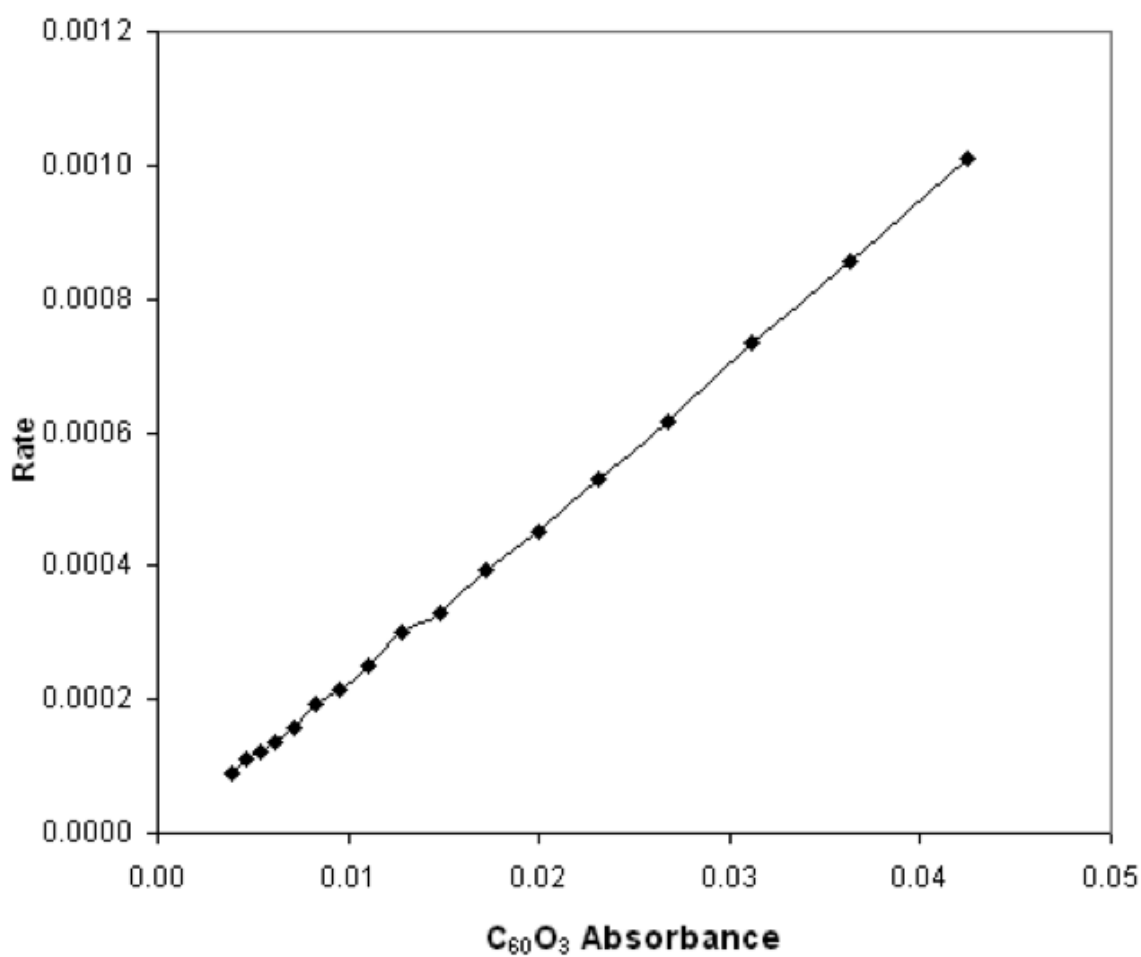


Looking at Figure 2, we see that the slope of the graph changes over the course of time. We should not be surprised then that Figure 3 shows that the rate of the reaction decreases as the reaction proceeds. The reaction is at first very fast but then slows considerably as the reactant $C_{60}O_3$ is depleted.

The shape of the graph for rate versus time (Figure 3) is very similar to the shape of the graph for concentration versus time (Figure 2). This suggests

that the rate of the reaction is related to the concentration of $C_{60}O_3$ at each time. Therefore, in Figure 4, we plot the rate of the reaction, defined in Equation (1) and shown in Figure 3, versus the absorbance of the $C_{60}O_3$.

Figure 4
Rate versus Concentration

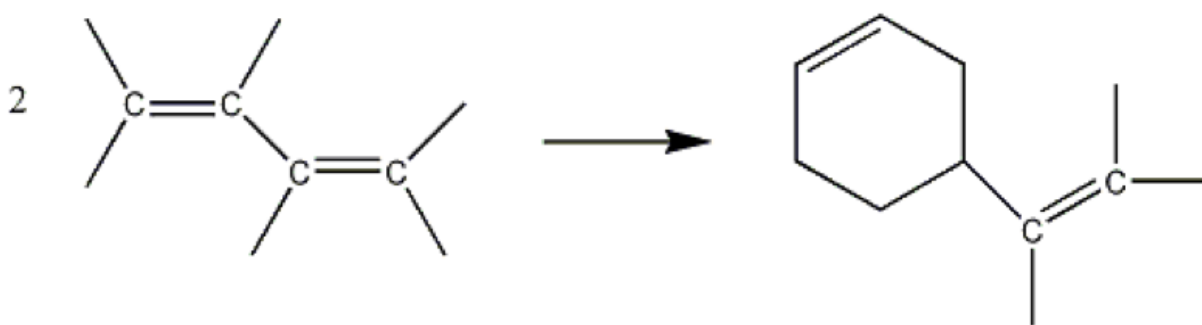


We find that there is a very simple proportional relationship between the rate of the reaction and the concentration of the reactant. Therefore, we can write

$$Rate = \frac{d[C_{60}O_3]}{dt} = k[C_{60}O_3]$$

where k is a proportionality constant. This equation shows that, early in the reaction when $[C_{60}O_3]$ is large, the reaction proceeds rapidly. As $C_{60}O_3$ is consumed, the reaction slows down. Equation (2) is an example of a “rate law,” expressing the relationship between the rate of a reaction and the concentrations of the reactant or reactants. Rate laws are expressions of the relationship between experimentally observed rates and concentrations.

As a second example of a reaction rate, we consider the “dimerization reaction” of butadiene gas, $CH_2=CH-CH=CH_2$. Two butadiene molecules can combine to form vinylcyclohexene, shown in Figure 5.



Dimerization of Butadiene to Vinylcyclohexene

Table 2 provides experimental data on the gas phase concentration of butadiene $[C_4H_6]$ as a function of time at $T = 250\text{ }^{\circ}\text{C}$.

We can estimate the rate of reaction at each time step as in Equation (1), and these data are presented in Table 2 as well. Again we see that the rate of reaction decreases as the concentration of butadiene decreases. This suggests that the rate is given by an expression like Equation (2). To test this, we calculate $Rate/[C_4H_6]$ in Table 2 for each time step. We note that this is not a constant, so the relationship in Equation (2) does not describe the relationship between the rate of reaction and the concentration of

butadiene. We can try a variety of different functions to find one which does describe the data. In Table 2, we calculate $Rate/[C_4H_6]^2$ to see if the relationship is an inverse square. We discover that this ratio is a constant throughout the reaction.

Time (sec)	[C ₄ H ₆] (M)	Rate (M/sec)	Rate/[C ₄ H ₆]	Rate/[C ₄ H ₆] ²
0	0.0917	9.48×10 ⁻⁶	1.03×10 ⁻⁴	1.13×10 ⁻³
500	0.0870	8.55×10 ⁻⁶	9.84×10 ⁻⁵	1.13×10 ⁻³
1000	0.0827	7.75×10 ⁻⁶	9.37×10 ⁻⁵	1.13×10 ⁻³
1500	0.0788	7.05×10 ⁻⁶	8.95×10 ⁻⁵	1.14×10 ⁻³
2000	0.0753	6.45×10 ⁻⁶	8.57×10 ⁻⁵	1.14×10 ⁻³
2500	0.0720	5.92×10 ⁻⁶	8.22×10 ⁻⁵	1.14×10 ⁻³
3000	0.0691	5.45×10 ⁻⁶	7.90×10 ⁻⁵	1.14×10 ⁻³
3500	0.0664	5.04×10 ⁻⁶	7.60×10 ⁻⁵	1.14×10 ⁻³
4000	0.0638	4.67×10 ⁻⁶	7.32×10 ⁻⁵	1.15×10 ⁻³

Dimerization of Butadiene at 250 °C

Therefore, the relationship between the rate of the reaction and the concentration of the reactant in this case is given by

$$Rate = \frac{d[C_4H_6]}{dt} = k[C_4H_6]^2$$

which is the rate law for the reaction in Figure 5. This is a very interesting result when compared to Equation (2). In both cases, the results show that the rate of reaction depends on the concentration of the reactant. However, we now also see that the way in which the rate varies with the concentration depends on what the reaction is. Each reaction has its own rate law, and this rate law must be measured and determined experimentally.

Observation 2: Rate laws and the order of reaction

We would like to understand what determines the specific dependence of the reaction rate on the reactant concentration in each reaction. In the first case considered above, the rate depends on the concentration of the reactant to the first power. We refer to this as a “first order reaction.” In the second case above, the rate depends on the concentration of the reactant to the second power, so this is called a “second order reaction.” There are also third order reactions, and even “zeroth order reactions” whose rates do not depend on the amount of the reactant. We need more observations of rate laws for different reactions.

The approach used in the previous section to determine a reaction’s rate law is fairly clumsy and at this point difficult to apply. We consider here a more systematic approach. First, consider the decomposition of $\text{N}_2\text{O}_5(\text{g})$.



We can create an initial concentration of N_2O_5 in a flask and measure the rate at which the N_2O_5 first decomposes. We can then create a different initial concentration of N_2O_5 and measure the new rate at which the N_2O_5 decomposes. By comparing these rates, we can find the order of the decomposition reaction. The rate law for decomposition of $\text{N}_2\text{O}_5(\text{g})$ is of the general form:

$$\text{Rate} = k[\text{N}_2\text{O}_5]^m$$

so we need to determine the exponent m . For example, at 25 °C we observe that the rate of decomposition is 1.4×10^{-3} M/s when the concentration of N_2O_5 is 0.020 M. If instead we begin with $[\text{N}_2\text{O}_5] = 0.010$ M, we observe

that the rate of decomposition is $7.0 \times 10^{-4} \text{ M/s}$. We can compare the rate from the first measurement $Rate(1)$ to the rate from the second measurement $Rate(2)$. From Equation (4), we can write that

$$\frac{Rate(1)}{Rate(2)} = \frac{k[N_2O_5]_1^m}{k[N_2O_5]_2^m} = \frac{1.4 \times 10^{-3} \text{ M/s}}{7.0 \times 10^{-4} \text{ M/s}} = \frac{k(0.020 \text{ M})^m}{k(0.010 \text{ M})^m}$$

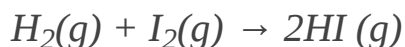
This can be simplified on both sides of the equation to give

$$2.0 = (2.0)^m$$

Clearly, then $m = 1$, and the decomposition is a first order reaction. We can also then find the first order rate constant k for this reaction by simply plugging in one of the initial rate measurements to Equation (4). We find that $k = 0.070 \text{ s}^{-1}$.

This approach to finding the reaction order is called the Method of Initial Rates, since it relies on fixing the concentration at specific initial values and measuring the initial rate associated with each concentration.

So far we have considered only reactions that have a single reactant. Consider a second example of the Method of Initial Rates involving the reaction of hydrogen gas and iodine gas:



In this case, we expect to find that the rate of the reaction depends on the concentrations for both reactants. As such, we need more initial rate observations to determine the rate law. In Table 3, observations are reported for the initial rate for three sets of initial concentrations of H_2 and I_2 .

Experiment	$[H_2]_0 \text{ (M)}$	$[I_2]_0 \text{ (M)}$	Rate (M/sec)
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Experiment	[H ₂] ₀ (M)	[I ₂] ₀ (M)	Rate (M/sec)
1	0.10	0.10	3.00×10 ⁻⁴
2	0.20	0.10	6.00×10 ⁻⁴
3	0.20	0.20	1.19×10 ⁻³

H₂ + I₂ initial rate data at 700 K

Following the same process we used in the N₂O₅ example, we write the general rate law for the reaction as

$$\text{Rate} = k[\text{H}_2]^n[\text{I}_2]^m$$

By comparing experiment 1 to experiment 2, we can write

$$\frac{\text{Rate}(1)}{\text{Rate}(2)} = \frac{k[\text{H}_2]_1^n[\text{I}_2]_1^m}{k[\text{H}_2]_2^n[\text{I}_2]_2^m} = \frac{3.00 \times 10^{-4} \text{ M/s}}{6.00 \times 10^{-4} \text{ M/s}} = \frac{k(0.10 \text{ M})^m(0.10)^n}{k(0.20 \text{ M})^m(0.10)^n}$$

This simplifies to (0.50) = (0.50)^m(1.00)ⁿ from which it is clear that $m = 1$. Similarly, we can find that $n = 1$. The reaction is therefore first order with respect to each reactant and is second order overall.

$$\text{Rate} = k[\text{H}_2][\text{I}_2]$$

Once we know the rate law, we can use any of the data from Table 3 to determine the rate constant, simply by plugging in concentrations and rate into Equation (9). We find that $k = 3.00 \times 10^{-2} \text{ /M} \cdot \text{sec}$.

This procedure can be applied to any number of reactions. The challenge is preparing the initial conditions and precisely measuring the initial change in concentration versus time. Table 4 provides an overview of the rate laws for several reactions. A variety of reaction orders are observed, and they cannot be easily correlated with the stoichiometry of the reaction.

Reaction	Rate Law
$2\text{NO}(\text{g}) + \text{O}_2 \rightarrow 2\text{NO}_2(\text{g})$	$\text{Rate} = k[\text{NO}]^2[\text{O}_2]$
$2\text{NO}(\text{g}) + 2\text{H}_2 \rightarrow 2\text{N}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g})$	$\text{Rate} = k[\text{NO}]^2[\text{H}_2]$
$2\text{ICl}(\text{g}) + \text{H}_2 \rightarrow 2\text{HCl}(\text{g}) + \text{I}_2\text{O}(\text{g})$	$\text{Rate} = k[\text{ICl}][\text{H}_2]$
$2\text{N}_2\text{O}_5(\text{g}) \rightarrow 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$	$\text{Rate} = k[\text{N}_2\text{O}_5]$
$2\text{NO}_2(\text{g}) + \text{F}_2(\text{g}) \rightarrow 2\text{NO}_2\text{F}(\text{g})$	$\text{Rate} = k[\text{NO}_2][\text{F}_2]$
$2\text{H}_2\text{O}_2(\text{aq}) \rightarrow 2\text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g})$	$\text{Rate} = k[\text{H}_2\text{O}_2]$
$\text{H}_2(\text{g}) + \text{Br}_2(\text{g}) \rightarrow 2\text{HBr}(\text{g})$	$\text{Rate} = k[\text{H}_2][\text{Br}_2]^{1/2}$
$\text{O}_3(\text{g}) + \text{Cl}(\text{g}) \rightarrow \text{O}_2(\text{g}) + \text{ClO}(\text{g})$	$\text{Rate} = k[\text{O}_3][\text{Cl}]$

Rate Laws for Various Reactions

Observation 3: Concentrations as a function of time and the reaction half-life

Once we know the rate law for a reaction, we should be able to predict how fast a reaction will proceed. From this, we should also be able to predict how much reactant remains or how much product has been produced at any given time in the reaction. We will focus on the reactions with a single reactant to illustrate these ideas.

Let's consider a first order reaction illustrated by $A \rightarrow \text{products}$, where A is a typical reactant. The rate law must be

$$\text{Rate} = -\frac{d[A]}{dt} = k[A]$$

From Calculus, it is possible to integrate Equation (10) to find the function $[A](t)$, which tells us the concentration $[A]$ as a function of time. The result

is

$$[A] = [A]_0 e^{-kt}$$

or equivalently

$$\ln[A] = \ln[A]_0 - kt$$

Equation (12) reveals that, if a reaction is first order, we can plot $\ln[A]$ versus time and get a straight line with slope equal to $-k$. This would be a way to test whether a reaction is first order or not. Moreover, if we know the rate constant and the initial concentration, we can predict the concentration at any time during the reaction.

An interesting point in the reaction is the time at which exactly half of the original concentration of A has been consumed. We call this time the “half-life” of the reaction and denote it as $t_{1/2}$. At that time, $[A] = [A]_0/2$. From Equation (12) and using the properties of logarithms, we find that, for a first order reaction

$$t_{1/2} = \frac{\ln 2}{k}$$

This equation tells us that the half-life of a first order reaction does not depend on how much material we start with. It takes exactly the same amount of time for the reaction to proceed from all of the starting material to half of the starting material as it does to proceed from half of the starting material to one-fourth of the starting material. In each case, we halve the remaining material in a time equal to the constant half-life in Equation (13).

These conclusions are only valid for first order reactions. Consider then a second order reaction, such as the butadiene dimerization discussed above. The general second order reaction $A \rightarrow \text{products}$ has the rate law

$$\text{Rate} = -\frac{d[A]}{dt} = k[A]^2$$

Again, we can use Calculus to find the function $[A](t)$ from Equation (14). The result is most easily written as

$$1/[A] = 1/[A]_0 + kt$$

Note that, as t increases, $1/[A]$ increases, so $[A]$ decreases. Equation (15) reveals that, for a reaction which is second order in the reactant A , we can plot $1/[A]$ as a function of time to get a straight line with slope equal to k . This would be a way to test whether a reaction is second order. And, if we know the rate constant and the initial concentration, we can find the concentration $[A]$ at any time of interest during the reaction.

The half-life of a second order reaction differs from the half-life of a first order reaction. From Equation (15), if we take $[A] = [A]_0/2$, we get

$$t_{1/2} = 1/k[A]_0$$

This shows that, unlike a first order reaction, the half-life for a second order reaction depends on how much material we start with. From Equation (16), the more concentrated the reactant is, the shorter the half-life.

These data tell us a great deal about how reaction rates depend on concentrations, but they do not tell us why they depend on concentrations, and in particular, they do not tell us why the exponents on the concentrations differ from one reaction to another and one reactant to another. In the next Concept Development Study, we will develop a model to account for this data.

Review and Discussion Questions

1. When $C_{60}O_3$ in toluene solution decomposes, O_2 is released leaving $C_{60}O$ in solution.
 - a. Based on the data in Figures 2 and 3, plot the concentration of $C_{60}O$ as a function of time. How would you define the rate of the reaction in terms of the slope of the graph in part (a)?
 - b. How is the rate of appearance of $C_{60}O$ related to the rate of disappearance of $C_{60}O_3$? Based on this, plot the rate of appearance of $C_{60}O$ as a function of time.
2. The reaction $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$ was found in this study to have rate law given by $k[N_2O_5]$ with $k=0.070s^{-1}$.

- a. How is the rate of appearance of NO_2 related to the rate of disappearance of N_2O_5 ? Which rate is larger?
 - b. Based on the rate law and rate constant, sketch a plot of $[\text{N}_2\text{O}_5]$, $[\text{NO}_2]$, and $[\text{O}_2]$ versus time all on the same graph.
3. Consider two decomposition reactions for two hypothetical materials, A and B. The decomposition of A is found to be first order, and the decomposition of B is found to be second order.
 - a. Assuming that the two reactions have the same rate constant at the same temperature, sketch $[\text{A}]$ and $[\text{B}]$ versus time on the same graph for the same initial conditions, i.e. $[\text{A}]_0 = [\text{B}]_0$.
 - b. Compare the half-lives of the two reactions. Under what conditions will the half-life of B be less than the half-life of A? Under what conditions will the half-life of B be greater than the half-life of A?
4. We found that the rate law for the reaction $\text{H}_2 + \text{I}_2(\text{g}) \rightarrow 2\text{HI}(\text{g})$ is $\text{Rate} = k[\text{H}_2][\text{I}_2]$. Therefore, the reaction is *second order* overall but *first order* with respect to H_2 . Imagine that we start with $[\text{H}_2]_0 = [\text{I}_2]_0$ and we measure $[\text{H}_2]$ versus time. Will a graph of $\ln([\text{H}_2])$ versus time be linear or will a graph of $1/[\text{H}_2]$ versus time be linear? Explain your reasoning.

Reaction Kinetics

Introduction

In the previous study, we found that the rates of chemical reactions depend on the concentrations of the reactants, which is not a surprising outcome. However, when analyzed in detail using the concept of a “rate law,” the results are surprising. In particular, it is not at all obvious why the exponents on the concentrations in the rate laws differ as they do and do not always correspond to their stoichiometric coefficients in the balanced chemical equation. There is no obvious pattern from one reaction to the next, or even between reactants in a single reaction. We need to develop a model to understand the variations from one reaction to the next, and this requires us to understand why reaction rates are related to reactant concentrations.

We will find that many reactions proceed quite simply, with reactant molecules colliding and exchanging atoms. In other cases, we will find that the process of reaction can be quite complicated, involving many molecular collisions and rearrangements leading from reactant molecules to product molecules. The rate of the chemical reaction is determined by these steps.

It is a common observation that reactions tend to proceed more rapidly with increasing temperature. Similarly, cooling reactants can have the effect of slowing a reaction to a near halt. From our study of the Kinetic Molecular Theory of Gases, we recall that temperature is related to the kinetic energy of the particles, so it seems to make sense that increasing the energy by increasing the temperature would increase reaction rates. However, we also can remember that not all reactions are endothermic. Reactions can be exothermic or endothermic, so many reactions do not require a net input of energy. Why then would an exothermic reaction speed up when the temperature is higher? We need to understand the role of energy in the reaction rate.

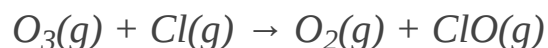
Foundation

In this study, we will rely on our understanding of the postulates and conclusions of the Kinetic Molecular Theory, including the relationship of temperature to kinetic energy and the model of gas molecules moving independently but occasionally colliding. We will of course assume we have measured and observed reaction rate laws in the previous study. We will also rely on our understanding of bonding and bond energies, specifically as they relate to the energies of chemical processes.

Observation 1: Collision Model for Simple Reactions

In the previous study, we observed the dependence of reaction rates on the concentration of reactants, and we have fit these data to equations called rate laws. Although this is very convenient, it does not provide us insight into why a particular reaction has a specific rate law.

To begin building our model to understand the concentration dependence of a reaction rate law, we consider a very simple reaction between two molecules in which a single atom is transferred between the molecules during the reaction. Our example is a reaction important in the decomposition of atmospheric ozone O_3 by aerosols:



$$Rate = k[O_3][Cl]$$

What must happen for a reaction to occur between an O_3 molecule and a Cl atom? Obviously, for these two particles to react, they must come into close proximity to one another so that an O atom can be transferred from one to the other. In general, two molecules cannot trade atoms to produce new product molecules unless they are close enough together for the atoms of the two molecules to interact. Although technically this is just a close encounter, chemists commonly refer to this as a collision between molecules.

Since the molecules must collide to react, the rate of the reaction cannot be any faster than the rate of collisions. This means that, for a reaction to occur quickly, the reacting molecules must collide frequently. We can also reason

that the rate of collisions must depend on the concentrations of the reactants. The more molecules there are in a confined space, the more likely they are to run into each other. To write this relationship in an equation, we can think in terms of probability, and we consider the reaction above. The probability for an O_3 molecule to be near a specific point increases with the number of O_3 molecules, and therefore increases with the concentration of O_3 molecules. The probability for a Cl atom to be near that specific point is also proportional to the concentration of Cl atoms. For an O_3 molecule and a Cl atom to collide, we need both to be in the same place at the same time. Remember that the probability of two things happening is the product of the probability of the first event times the probability for the second event. Therefore, the probability for an O_3 molecule and a Cl atom to be in close proximity to the same specific point at the same time is proportional to the $[\text{O}_3] \times [\text{Cl}]$.

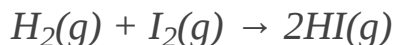
It is important to remember that not all collisions between O_3 molecules and Cl atoms will result in a reaction. There are other factors to consider including how the molecules approach one another. The atoms may not be positioned properly to exchange between molecules, in which case the molecules will simply bounce off of one another without reacting. For example, if the Cl atom approaches the center O atom of the O_3 molecule, that O atom will not transfer. Another factor is the energy associated with the reaction. As we said above, though, a collision must occur for the reaction to occur, and therefore there rate of the reaction can be no faster than the rate of collisions between the reactant molecules.

Therefore, we can say that, in a *bimolecular reaction* where two molecules collide and react, the rate of the reaction will be proportional to the product of the concentrations of the reactants. For the reaction of O_3 with Cl, the rate must therefore be proportional to $[\text{O}_3] \times [\text{Cl}]$, and this is exactly what we observe in the experimental rate law in Equation (2). Thus, it appears that we can understand the concentration dependence of the rate law by understanding the collisions that must occur for the reaction to take place.

As a cautionary note, the results from the previous Concept Development Study make it clear that not every rate law is as simple as the one for the reaction of O_3 with Cl. We will return to this topic in a later section.

Observation 2: Temperature Dependence of Reaction Rates

How is the effect of temperature change on the reaction rate reflected in the rate law equation? Recall that a rate law shows the dependence of the reaction rate on reactant concentrations, e.g. the rate of reaction of I₂ gas with H₂ as described in Equation (3) is given by the rate law in Equation (4).



$$\text{Rate} = k[\text{H}_2][\text{I}_2]$$

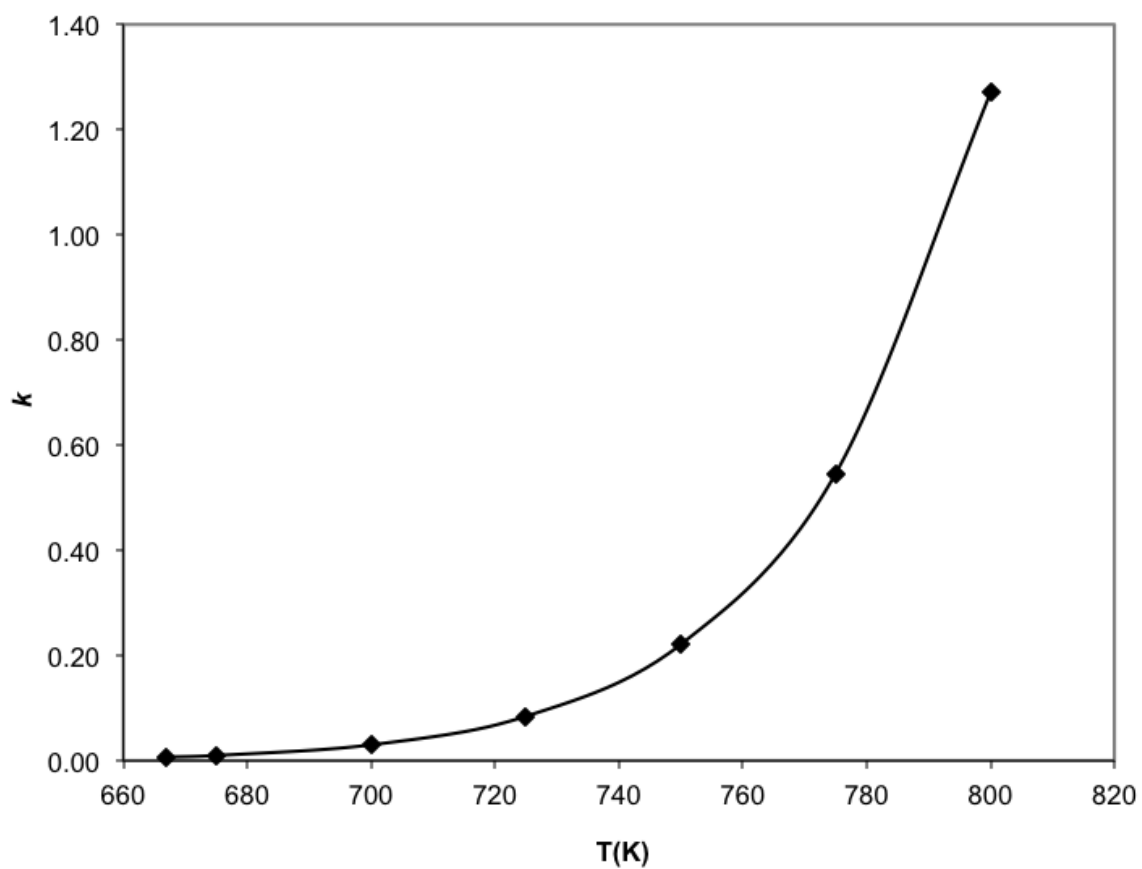
One possibility for the increase in the rate of this reaction when temperature is increased is that there is a slight dependence on temperature of the concentrations, since volumes do vary with temperature. However, this is insufficient to account for the dramatic changes in rate typically observed. Therefore, the temperature dependence of the reaction rate is primarily found in the rate constant, k . The rate constant of this reaction at each temperature can be found using the Method of Initial Rates, as discussed in the previous study, and we find in Table 1 that the rate constant increases dramatically as the temperature increases.

T(K)	k (1/M·sec)
667	6.8×10^{-3}
675	9.87×10^{-3}
700	3.00×10^{-2}
725	8.43×10^{-2}

T(K)	k (1/M·sec)
750	2.21×10^{-1}
775	5.46×10^{-1}
800	1.27

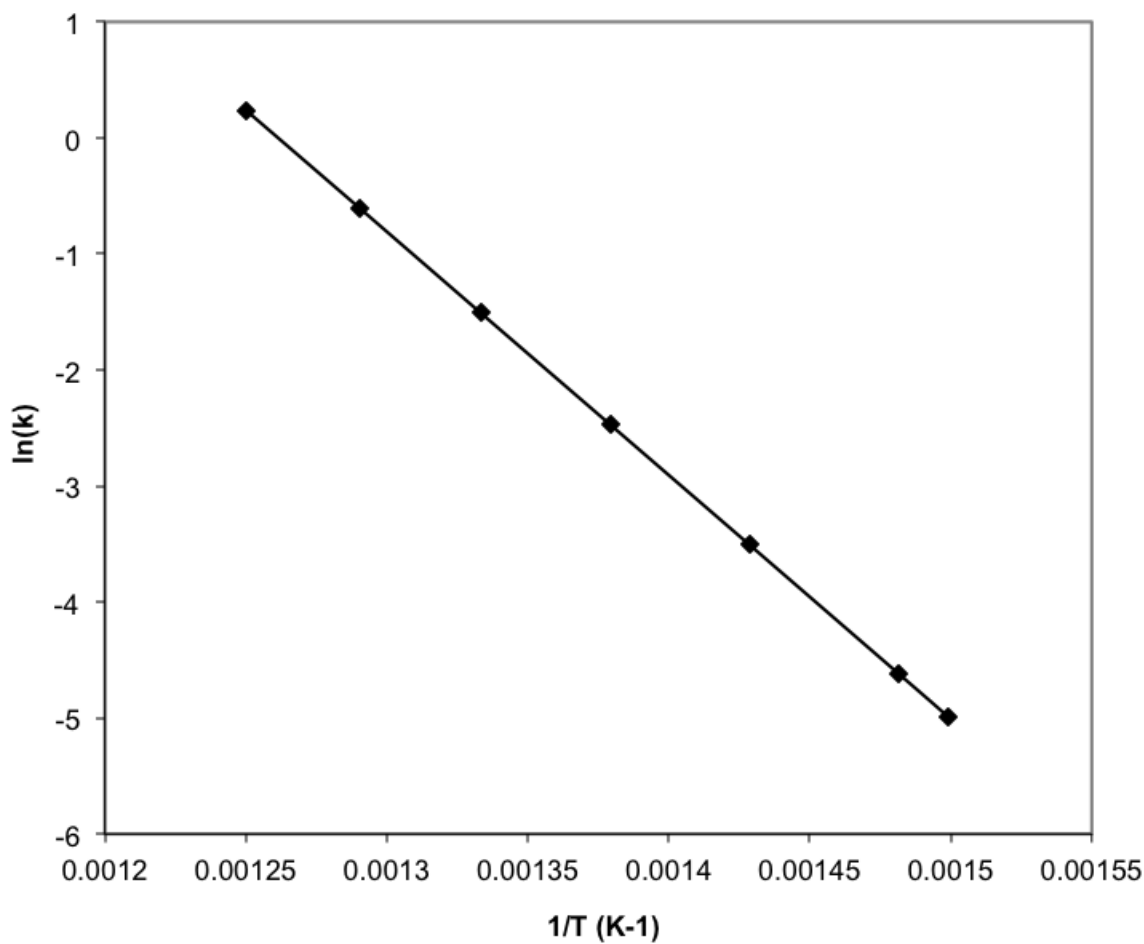
Rate constant for H_2 (g) + I_2 (g)

Figure 1
Rate Constant



As shown in Figure 1, the rate constant appears to increase exponentially with temperature. After a little experimentation with the data, we find in Figure 2 that there is a simple linear relationship between $\ln(k)$ and $1/T$.

Figure 2
Rate Constant



From Figure 2, we can see that the data in Table 1 fit the equation

$$\ln(k) = a \frac{1}{T} + b$$

where a and b are constant for this reaction. It turns out that, for our purposes, all reactions have rate constants that fit Equation (5), but with different constants a and b for each reaction. Figure 2 is referred to as an Arrhenius plot, after Svante Arrhenius.

It is not obvious why this equation should work for every chemical reaction. When we remember that the temperature is related to energy, it would seem that exothermic reactions and endothermic reactions should have different temperature dependence. Since they do not, this suggests that temperature increases and corresponding energy increases are not connected to the overall energy change of a reaction. This will lead us to a model to account for the temperature dependence of the rate constant. We will develop this further later in the next section.

Observation 3: Activation Energy

Equation (5) is very convenient for describing the temperature dependence of a reaction. However, we would like some insight into why the temperature dependence should obey Equation (5), and in particular, into the meaning of the constants a and b in the equation.

As noted at the end of the last section, Equation (5) describes the rate constant temperature dependence regardless of whether the reaction is endothermic or exothermic. Therefore, whatever the energetic factor is that is required for the reaction to occur, it is not just that the reaction is endothermic. Exothermic reactions apparently require energy as well. It must be that all reactions, regardless of the overall change in energy, require energy to occur.

A model to account for this is the concept of “activation energy.” For a reaction to occur, at least some bonds in the reactant molecule must be broken, so that atoms can rearrange and new bonds can be created. At the time of collision, bonds are stretched and broken as new bonds are made. For example, in the reaction in Equation (1), $O_3(g) + Cl(g) \rightarrow O_2(g) + ClO(g)$, one of the O-O bonds in O_3 does not exist after the reaction. Breaking reactant bonds and rearranging the atoms during the collision

requires the input of energy. The minimum amount of energy required for the reaction to occur is called the activation energy, E_a .

This idea is illustrated in Figure 3, showing conceptually how the energy of the reactants varies as the reaction proceeds. In Figure 3a, the energy is low early in the reaction, when the molecules are still arranged as reactants. As the molecules approach and begin to rearrange, the energy rises sharply, rising to a maximum in the middle of the reaction. This sharp rise in energy is the activation energy, as illustrated. After the middle of the reaction has passed and the molecules are arranged more as products than reactants, the energy begins to fall again. However, the energy does not fall to its original value, so this is an endothermic reaction.

Figure 3b shows the analogous situation for an exothermic reaction. Again, as the reactants approach one another, the energy rises as the atoms begin to rearrange. At the middle of the collision, the energy maximizes and then falls as the product molecules form. In an exothermic reaction, the product energy is lower than the reactant energy.

Figure 3 thus shows that an energy barrier must be surmounted for the reaction to occur, regardless of whether the energy of the products is greater than (Figure 3a) or less than (Figure 3b) the energy of the reactants. This barrier accounts for the temperature dependence of the reaction rate. We know from the Kinetic Molecular Theory that as temperature increases the average energy of the molecules in a sample increases. Therefore, as temperature increases, the fraction of molecules with sufficient energy to surmount the reaction activation barrier increases.

Figure 3a
Reaction Energy

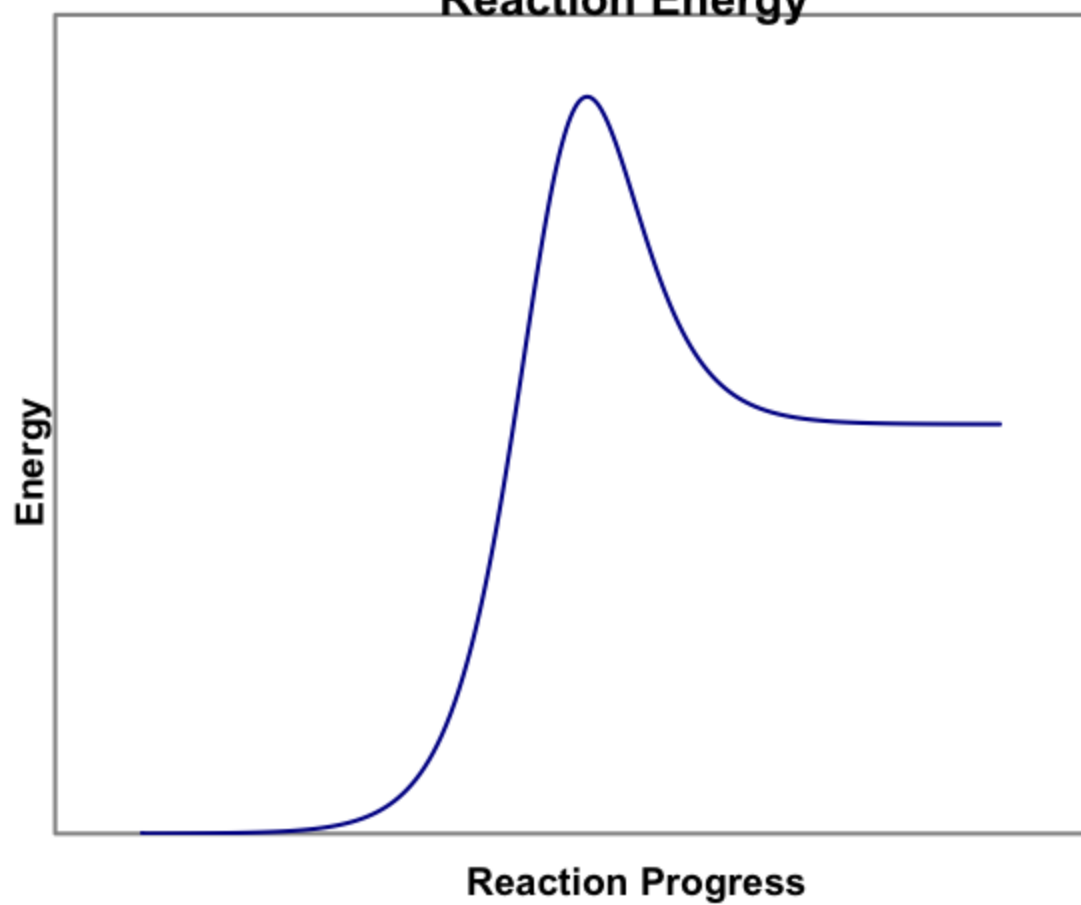
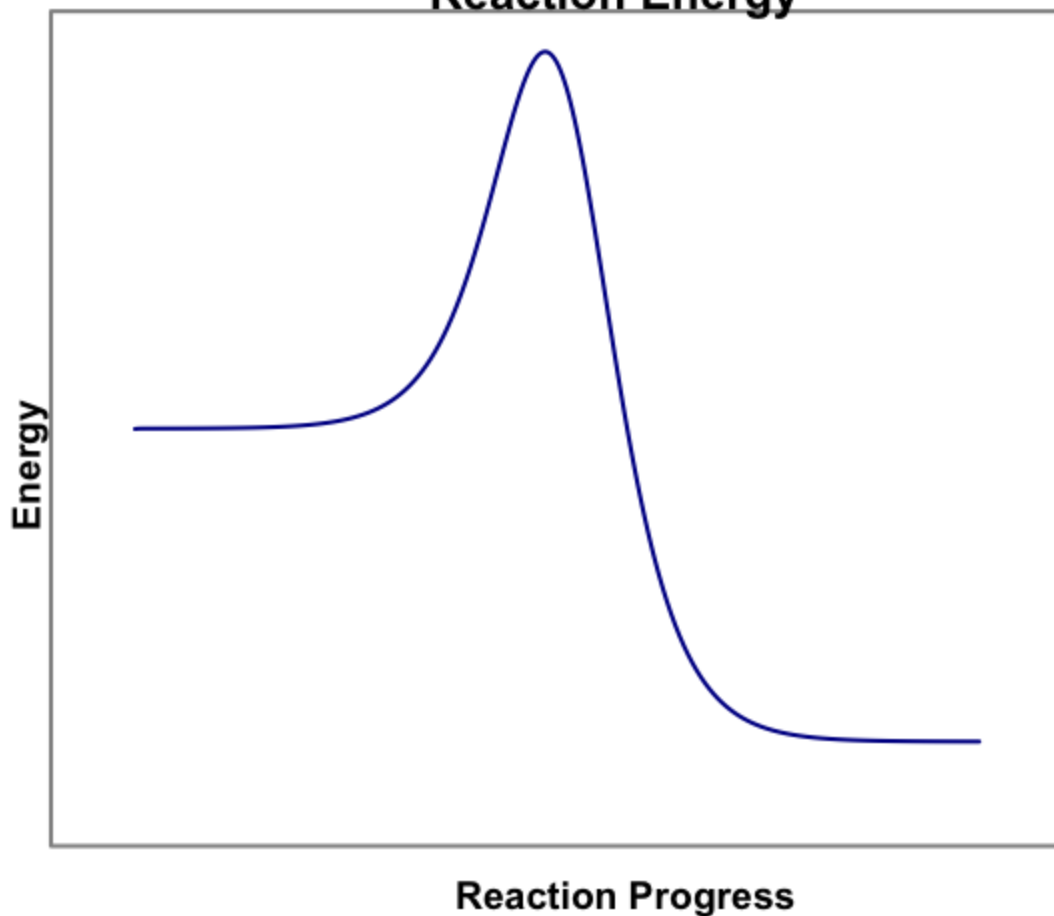


Figure 3b
Reaction Energy



Although we will not show it here, the Kinetic Molecular Theory shows that the fraction of molecules with energy greater than E_a at temperature T is proportional to $e^{-E_a/RT}$. This means that the reaction rate and therefore also the rate constant must be proportional to $e^{-E_a/RT}$. Therefore we can write

$$k(T) = Ae^{-E_a/RT}$$

where A is a new proportionality constant. If we take the logarithm of both sides of Equation (7), we find that

$$\ln k(T) = -E_a/RT + \ln A$$

This equation matches the experimentally observed Equation (5). We recall that a graph of $\ln(k)$ versus $1/T$ is observed to be linear. Now we see that the slope of that graph is equal to $-E_a/R$.

We might think that the activation energy for a reaction is the energy required to break one or more bonds in the reactants. Looking back at Reaction (1) between a Cl atom and an O_3 molecule, we would predict that the activation energy would be equal to the bond energy for breaking one of the O-O bonds in O_3 , which is equal to 400 kJ/mol. However, the activation energy for Reaction (1) has been experimentally found to be 2.1 kJ/mol, enormously less than the energy required to break the O-O bond. How can this be?

The answer must be that the O-O bond does not break to create a free O atom during this reaction. That must cost too much energy. Instead, the O atom is handed off in a single step between the O_2 and the Cl atom. The Cl-O bond is formed at the same instant that the O-O bond is broken. The bonding electrons rearrange from one bond to the other, so the electron energy is never raised by very much energy.

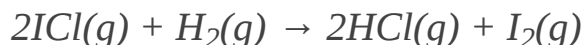
This is a lesson worth remembering. Activation energies and bond energies are not the same thing. In general, activation energies are much, much lower than bond energies, so reactions do not typically occur by consecutively breaking the reactant bonds and then forming the product bonds.

As a final note on Equation (7), the constant A must have some physical significance. We have accounted for the probability of collision between two molecules and we have accounted for the energetic requirement for a successful reactive collision. We have not accounted for the probability that a collision will have the appropriate orientation of reactant molecules during the collision. Moreover, not every collision that occurs with proper orientation and sufficient energy will actually result in a reaction. There are other random factors relating to the internal structure of each molecule at the instant of collision. The factor A takes accounts for all of these factors and is essentially the probability that a collision with sufficient energy for reaction will indeed lead to a reaction. A is commonly called the “frequency factor.”

Observation 4: Rate laws for more complicated reaction processes

Our collision model in the previous section accounts for the concentration and temperature dependence of the reaction rate, as expressed by the rate law. The concentration dependence arises from calculating the probability of the reactant molecules being in the same vicinity at the same instant. Therefore, we should be able to predict the rate law for any reaction by simply multiplying together the concentrations of all reactant molecules in the balanced stoichiometric equation. The order of the reaction should therefore be simply related to the stoichiometric coefficients in the reaction. However, the data in Table 4 of the previous study shows that this is incorrect for many reactions.

Consider, for example, the apparently simple reaction



Based on the collision model, we would assume that the reaction occurs by 2 ICl molecules colliding with a single H₂ molecule. The probability for such a collision should be proportional to [ICl]²[H₂]. However, we experimentally observe that the rate law for this reaction is

$$\text{Rate} = k[\text{ICl}][\text{H}_2]$$

As a second example, consider the reaction



It would seem reasonable to assume that this reaction occurs as a single collision in which an oxygen atom is exchanged between the two molecules. However, the experimentally observed rate law for this reaction is

$$\text{Rate} = k[\text{NO}_2]^2$$

In this case, [CO] does not affect the rate of the reaction at all, and [NO₂] is squared. These examples demonstrate that the rate law for a reaction cannot

always be predicted from the stoichiometric coefficients and therefore that the collision model often does not account for the rate of the reaction. There must be something seriously incomplete with the collision model.

The key assumption of the collision model is that the reaction occurs by a single collision. Since this assumption leads to incorrect predictions of rate laws in some cases, the assumption must be invalid in at least those cases. It may well be that reactions require more than a single collision to occur, even in reactions involving just two types of molecules as in Equation (10).

Moreover, if more than two molecules are involved as in Equation (8), the chance of a single collision involving all of the reactive molecules becomes very small. It is hard enough to get two particles to collide and react. It is much less probable that three particles will collide simultaneously to react in a single step.

We conclude that many reactions, including those in Equations (8) and (10), must occur as a result of several collisions occurring in sequence, rather than a single collision. The rate of the chemical reaction must be determined by the rates of the individual steps in the reaction.

Each step in a complex reaction is a single collision, often referred to as an “elementary process.” In a single collision process step, our collision model should correctly predict the rate of that step. The sequence of such elementary processes leading to the overall reaction is referred to as the “reaction mechanism.” Determining the mechanism for a reaction can require gaining substantially more information than simply the rate data we have considered here. However, we can gain some progress just from the rate law.

Consider, for example, the reaction in Equation (10) described by the rate law in Equation (11). Since the rate law involved $[\text{NO}_2]^2$, one step in the reaction mechanism must involve the collision of two NO_2 molecules since the probability of such a collision would be proportional to $[\text{NO}_2]^2$.

Eventually, the CO reactant molecule must come into play in the reaction, so we would think that $[\text{CO}]$ would have to be included in the rate law. But this is not the experimental result. This means that the rate of the reaction

depends only on how fast the reaction between the two NO_2 molecules occurs. That one step must determine the rate of the overall reaction. Why would that be?

In any multi-step process, if one step is considerably slower than all of the other steps, the rate of the multi-step process is determined entirely by that slowest step, because the overall process cannot go any faster than the slowest step. It does not matter how rapidly the rapid steps occur. Therefore, the slowest step in a multi-step process is called the “rate determining” or “rate limiting” step.

This argument suggests that the reaction in Equation (10) proceeds via a slow step in which two NO_2 molecules collide, followed by at least one other rapid step leading to the products. A possible mechanism is therefore

Step 1: $\text{NO}_2 + \text{NO}_2 \rightarrow \text{NO}_3 + \text{NO}$ *slow*

Step 2: $\text{NO}_3 + \text{CO} \rightarrow \text{NO}_2 + \text{CO}_2$ *fast*

If Step 1 is much slower than Step 2, the rate of the reaction is entirely determined by the rate of Step 1. From our collision model, the rate law for Step 1 must be $\text{Rate} = k[\text{NO}_2]^2$, which is consistent with the experimentally observed rate law for the overall reaction. This suggests that the mechanism in Equations (12a) and (12b) is the correct description of the reaction process for Reaction (10), with the first step as the rate determining step.

There are a few important notes about the mechanism. First, one product of the reaction is produced in the first step, and the other is produced in the second step. Therefore, the mechanism does lead to the overall reaction, consuming the correct amount of reactant and producing the correct amount of product. Second, the first reaction produces a new molecule, NO_3 , which is neither a reactant nor a product. The second step then consumes that molecule, and NO_3 therefore does not appear in the overall reaction, Equation (10). As such, NO_3 is called a “reaction intermediate.” Intermediates play important roles in the rates of many reactions.

If the first step in a mechanism is rate determining as in this case, it is easy to find the rate law for the overall expression from the mechanism. If the

second step or later steps are rate determining, determining the rate law is slightly more involved. The process for finding the rate law in such a case is illustrated in Discussion Question 7.

Review and Discussion Questions

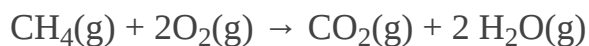
1. For the reactions listed in Table 4 of the previous concept development study, which of these can you be certain that the reaction does not occur as a single step collision? Explain your reasoning.
2. A graph of the logarithm of the equilibrium constant for a reaction versus $1/T$ is linear but can have either a negative slope or a positive slope, depending on the reaction, as was observed in Concept Development Study 12. However, the graph of the logarithm of the rate constant for a reaction versus $1/T$ has a negative slope for essentially every reaction. Using equilibrium arguments, explain why the graph for the rate constant must have a negative slope.
3. Using Equation (18) and the data in Table 5, determine the activation energy for the reaction $H_2(g) + I_2 \rightarrow 2HI(g)$.
4. As a rough estimate, chemists often assume a “rule of thumb” that the rate of any reaction will double when the temperature is increased by 10°C .
 - a. What does this suggest about the activation energies of reactions?
 - b. Using Equation (18), calculate the activation energy of a reaction whose rate doubles when the temperature is raised from 25°C to 35°C .
 - c. Does this “rule of thumb” estimate depend on the temperature range? To find out, calculate the factor by which the rate constant increases when the temperature is raised from 100°C to 110°C , assuming the same activation energy you found in part (b). Does the rate double in this case?
5. Consider a very simple hypothetical reaction which comes to equilibrium.
 - a. At equilibrium, what must be the relationship between the rate of the forward reaction, and the reverse reaction ?

- b. Assume that both the forward and reverse reactions are elementary processes occurring by a single collision. What is the rate law for the forward reaction? What is the rate law for the reverse reaction?
 - c. Using the results of (a) and (b), show that the equilibrium constant for this reaction can be calculated from k_f , where k_f is the rate constant for the forward reaction and k_r is the rate constant for the reverse reaction.
6. Consider a very simple hypothetical reaction $A + B \leftrightarrow C + D$. By examining Figure 8, provide and explain the relationship between the activation energy in the forward direction, $E_{a,f}$ and in the reverse direction, $E_{a,r}$. Does this relationship depend on whether the reaction is endothermic (Figure 8a) or exothermic (Figure 8b)? Explain.
7. For the reaction $H_2(g) + I_2(g) \rightarrow 2HI(g)$, the rate law is $Rate = k[H_2][I_2]$. Although this suggests that the reaction is a one-step elementary process, there is evidence that the reaction occurs in two steps, and the second step is the rate determining step: Step 1: $I_2 \leftrightarrow 2I$ (fast) Step 2: $H_2 + 2I \rightarrow 2HI$ (slow)
 - a. If both the forward and reverse reactions in step 1 are much faster than step 2, explain why step 1 can be considered to be at equilibrium.
 - b. What is the rate law for the rate determining step?
 - c. Since the rate law in (b) depends on the concentration of an intermediate I, we need to find that intermediate. Calculate [I] from Step 1, assuming that Step 1 is at equilibrium.
 - d. Substitute [I] from part (c) into the rate law in part (b) to find the overall rate law for the reaction. Is this result consistent with the experimental observation?

Reaction Equilibrium in the Gas Phase

Introduction

We performed “chemical algebra” or stoichiometric calculations in the early Concept Development Studies, using a balanced chemical equation to determine the masses or numbers of moles of product created from the masses or numbers of moles of the reactants. For example, if we burn methane gas, $\text{CH}_4(\text{g})$, in excess oxygen, the reaction



occurs, and we assumed, correctly in this case, that the number of moles of $\text{CO}_2(\text{g})$ produced is equal the number of moles of $\text{CH}_4(\text{g})$ we start with. This follows directly from the balanced equation but requires us to assume that all of the CH_4 is converted into CO_2 during the reaction.

From our study of phase transitions and solubility, we have learned the concept of equilibrium. We observed that, in the transition from one phase to another for a substance, both phases are found to coexist under certain conditions, and we refer to this as phase equilibrium. For example, when a liquid is in equilibrium with its vapor, not all of the liquid converts into vapor and not all of the vapor converts into the liquid. In this case, we would not be able to calculate the number of moles of vapor from the number of moles of liquid.

It should not surprise us that these same concepts of equilibrium used to describe the coexistence of phases can apply to chemical reactions as well. In Reaction (1) above, therefore, we should determine whether the reaction actually produces exactly one mole of CO_2 for every mole of CH_4 we start with or whether we wind up with an equilibrium mixture containing both CO_2 and CH_4 . In this case, the answer is that the reaction does “go to completion,” meaning that with very high accuracy we can assume that every CH_4 reacts to produce a CO_2 . However, in studying many reactions, we will find that different reactions provide us with varying outcomes. In many cases, virtually all reactants are consumed, producing the amount of product predicted by stoichiometric calculation. In many other cases, substantial amounts of reactant are still present along with product when the reaction achieves equilibrium. And in other cases, almost no product is present at equilibrium. Our goal will be to understand, describe, and predict the reaction equilibrium.

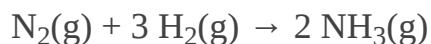
An important corollary to this goal is to attempt to control the equilibrium. We will find that varying the conditions under which the reaction occurs can vary the amounts of reactants and products present at equilibrium. We will develop a general principle for predicting how the reaction conditions affect the amount of product produced at equilibrium.

Foundation

In beginning our study of the reactions of gases, we will assume a knowledge of the physical properties of gases as described by the Ideal Gas Law and an understanding of these properties as given by the postulates and conclusions of the Kinetic Molecular Theory. We assume that we have developed a dynamic model of phase equilibrium in terms of competing rates. We will also assume an understanding of the bonding, structure, and properties of individual molecules.

Observation 1: Reaction equilibrium

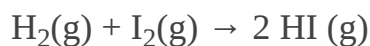
We begin by analyzing a significant industrial chemical process, the synthesis of ammonia gas, NH_3 , from nitrogen and hydrogen:



If we start with 1 mole of N_2 and 3 moles of H_2 , the balanced equation predicts that we will produce 2 moles of NH_3 . In fact, if we carry out this reaction starting with these quantities of nitrogen and hydrogen at 298 K in a 100.0 L reaction vessel, we observe that the number of moles of NH_3 produced is 1.91 mol. This “yield” is less than predicted by the balanced equation, but the difference is not due to a limiting reactant factor. Recall that, in stoichiometry, the limiting reactant is the one that is present in less than the ratio of moles given by the balanced equation. In this case, neither N_2 nor H_2 is limiting because they are present initially in a 1:3 ratio, exactly matching the stoichiometry. Note also that this seeming deficit in the yield is not due to any experimental error or imperfection, nor is it due to poor measurements or preparation. Rather, the observation is completely reproducible: every measurement of this reaction at this temperature in this volume starting with 1 mole of N_2 and 3 moles of H_2 produces 1.91 moles rather than 2 moles. We conclude that the Reaction (2) achieves *reaction equilibrium* in which all three gases are present in the gas mixture. We can determine the amounts of each gas at equilibrium from the stoichiometry of the reaction. When $n(\text{NH}_3) = 1.91$ mol are created, the number of moles of N_2 remaining at equilibrium is $n(\text{N}_2) = 0.045$ mol and $n(\text{H}_2) = 0.135$ mol.

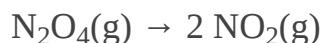
It is important to note that we can vary the relative amount of NH_3 produced by varying the temperature of the reaction, the volume of the vessel in which the reaction occurs, or the relative starting amounts of N_2 and H_2 . We shall study and analyze this observation in detail in later sections. For now, though, we demonstrate that the concept of reaction equilibrium is general to all reactions.

Consider the reaction



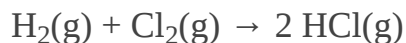
If we begin with 1.00 mole of H_2 and 1.00 mole of I_2 at 500 K in a reaction vessel of fixed volume, we observe that, at equilibrium, $n(\text{HI}) = 1.72$ mol, leaving in the equilibrium mixture $n(\text{H}_2) = 0.14$ mol and $n(\text{I}_2) = 0.14$ mol.

Similarly, consider the decomposition reaction



At 298 K in a 100.0 L reaction flask, 1.00 mole of N_2O_4 partially decomposes to produce, at equilibrium, $n(\text{NO}_2) = 0.64$ mol and $n(\text{N}_2\text{O}_4) = 0.68$ mol.

Some chemical reactions achieve an equilibrium that appears to be very nearly complete reaction. For example,



If we begin with 1.00 mole of H_2 and 1.00 mole of Cl_2 at 298 K in a reaction vessel of fixed volume, we observe that, at equilibrium, $n(\text{HCl})$ is almost exactly 2.00 mol, leaving virtually no H_2 or Cl_2 . This does not mean that the reaction has not come to equilibrium. It means instead that, at equilibrium, there are essentially no reactants remaining.

In each of these cases, the amounts of reactants and products present at equilibrium vary as the conditions are varied but are completely reproducible for fixed conditions. Before making further observations that will lead to a quantitative description of the reaction equilibrium, we consider a qualitative model of equilibrium.

We begin with a dynamic equilibrium description. We know from our studies of phase transitions that equilibrium occurs when the rate of the forward process (e.g. evaporation) is matched by the rate of reverse process (e.g. condensation). Since we have now observed that gas reactions also come to equilibrium, we should imagine that at equilibrium the forward reaction rate is equal to the reverse reaction rate. For

example, in Reaction (4) above, the rate of decomposition of N_2O_4 molecules at equilibrium must be exactly matched by the rate of recombination (or “dimerization”) of NO_2 molecules.

How can we show that this model is correct and the forward and reverse reactions continue to happen at equilibrium? We can do as we did in the case of phase equilibrium by varying the volume. With the $\text{NO}_2/\text{N}_2\text{O}_4$ mixture at equilibrium, we can vary the volume of the flask containing the mixture and determine what happens to the equilibrium. If we increase the volume and the reaction is allowed to come to equilibrium, we observe that the amount of NO_2 at equilibrium is larger and the amount of N_2O_4 is smaller. This shows that the amounts of the gases at equilibrium depend on the reaction conditions, including the volume. However, imagine that the forward and reverse reactions stop once the equilibrium amounts of material are achieved. If this were the case, the molecules would not “know” that the volume of the container had increased and there would be no change in the amounts of gas at equilibrium. Since the reaction equilibrium can and does respond to a change in volume, it must be that the change in volume affects the rates of both the forward and reverse processes. This means that both reactions must be occurring at equilibrium, and that their rates must exactly match at equilibrium.

This reasoning reveals that the amounts of reactant and product present at equilibrium are determined by the rates of the forward and reverse reactions. If the rate of the forward reaction (e.g. decomposition of N_2O_4) is faster than the rate of the reverse reaction, then at equilibrium we have more product than reactant. If that difference in rates is very large, at equilibrium there will be much more product than reactant. Of course, the converse of these conclusions is also true. It must also be the case that the rates of these processes depends on, amongst other factors, the volume of the reaction flask, since the amounts of each gas present at equilibrium change when the volume is changed.

Since we have studied how the rates of reactions depend on concentrations, we should be able to quantify these effects at equilibrium. First, however, we quantify the equilibrium itself.

Observation 2: Equilibrium constants

We observed that the equilibrium partial pressures of the gases in a reaction vary depending upon a variety of conditions. These include changes in the initial numbers of moles of reactants and products, changes in the volume of the reaction flask, and changes in the temperature. We now study these variations quantitatively.

Consider first Reaction (4) above, the decomposition of $\text{N}_2\text{O}_4(\text{g})$ to form $\text{NO}_2(\text{g})$:



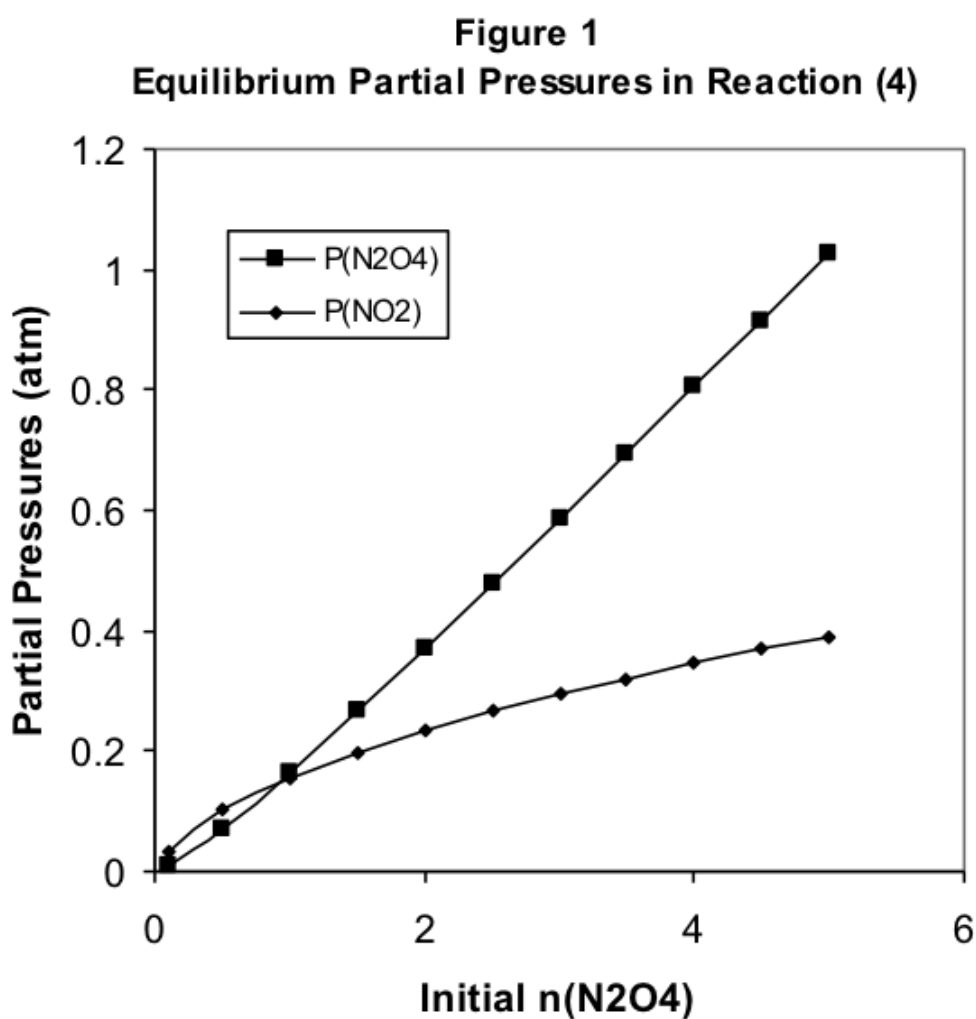
Following on our previous study of this reaction, we inject an initial amount of $\text{N}_2\text{O}_4(\text{g})$ into a 100 L reaction flask at 298 K. Now, however, we vary the initial number of moles of $\text{N}_2\text{O}_4(\text{g})$ in the flask and measure the equilibrium pressures of both the reactant and product gases. The results of a number of such studies are given in Table 1.

Initial n(N_2O_4)	P(N_2O_4) (atm)	P(NO_2) (atm)
0.1	0.00764	0.033627
0.5	0.07011	0.102517
1	0.166136	0.156806
1.5	0.26735	0.198917
2	0.371791	0.234574
2.5	0.478315	0.266065
3	0.586327	0.294578
3.5	0.695472	0.320827
4	0.805517	0.345277
4.5	0.916297	0.368255
5	1.027695	0.389998

Equilibrium Partial Pressures in Reaction (4)

The relationship between the pressures at equilibrium and the initial amount of N_2O_4 is perhaps more easily seen in a graph of the data in Table 1, as shown in Figure 1.

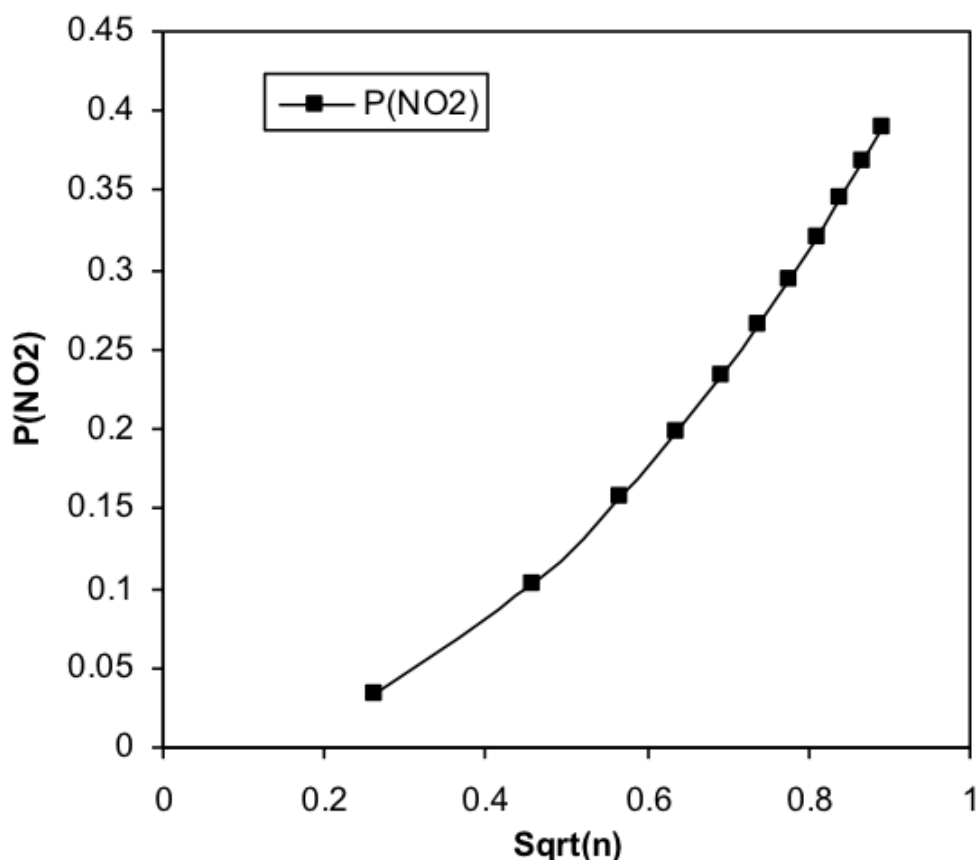
We might reasonably have predicted that the amount of NO_2 produced at equilibrium would increase in direct proportion to increases in the amount of N_2O_4 we begin with. Table 1 shows that this is definitely not the case. Note that when we increase the initial



amount of N_2O_4 by a factor of 10 from 0.5 moles to 5.0 moles, the pressure of NO_2 at equilibrium increases by a factor of less than 4.

There are some interesting observations here. Note that, when the initial amount of N_2O_4 is less than 1 mole, the equilibrium pressure of NO_2 is greater than that of N_2O_4 . These relative pressures reverse as the initial amount increases, with the N_2O_4 equilibrium pressure keeping track with the initial amount but the NO_2 pressure falling short. Clearly, the equilibrium pressure of NO_2 does not increase proportionally with the initial amount of N_2O_4 . In fact, the increase is slower than proportionality, suggesting perhaps a square root relationship between the pressure of NO_2 and the initial amount of N_2O_4 .

Figure 2
Relationship of $P(\text{NO}_2)$ to Initial $n(\text{N}_2\text{O}_4)$



We test this in Figure 2 by plotting $P(\text{NO}_2)$ at equilibrium versus the square root of the initial number of moles of N_2O_4 . Figure 2 makes it clear that this is not a simple proportional relationship, but it is closer. Note in Figure 1 that the equilibrium pressure $P(\text{N}_2\text{O}_4)$ increases near proportionally with the initial amount of N_2O_4 .

This suggests plotting $P(\text{NO}_2)$ versus the square root of $P(\text{N}_2\text{O}_4)$. This is done in Figure 3, where we discover that there is a very simple proportional relationship between the variables plotted in this way. We have thus observed that

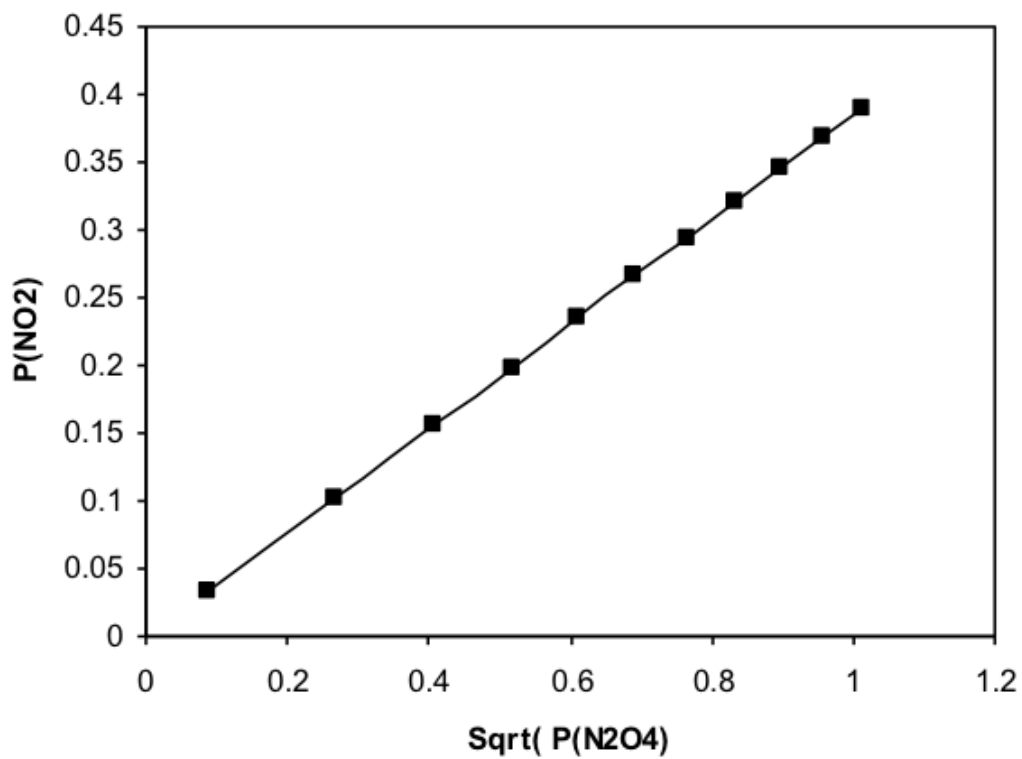
$$P(\text{NO}_2) = c\sqrt{P(\text{N}_2\text{O}_4)}$$

where c is the slope of the graph. Equation (8) can be rewritten in a form that chemists standardly use, where $c = K_p$:

$$K_p = \frac{P(\text{NO}_2)^2}{P(\text{N}_2\text{O}_4)}$$

To test the accuracy of this equation and to find the value of K_p , we return to Table 1 and add another column in which we calculate the value of K_p for each of the data points. Table 2 makes it clear that the “constant” in Equation 9 truly is independent of both the initial conditions and the equilibrium partial pressure of either one of the reactant or product. We thus refer to the constant K_p in Equation 9 as the “reaction equilibrium constant.”

Figure 3
Equilibrium Partial Pressures



Initial n(N ₂ O ₄)	P(N ₂ O ₄) (atm)	P(NO ₂) (atm)	K _p
0.1	0.00764	0.0336	0.148
0.5	0.0710	0.102	0.148
1	0.166	0.156	0.148
1.5	0.267	0.198	0.148
2	0.371	0.234	0.148

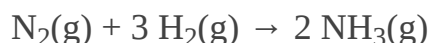
2.5	0.478	0.266	0.148
3	0.586	0.294	0.148
3.5	0.695	0.320	0.148
4	0.805	0.345	0.148
4.5	0.916	0.368	0.148
5	1.027	0.389	0.148

Equilibrium Partial Pressures in Reaction (4)

Recall that we have seen a reaction equilibrium constant before in our study of solubility. The solubility product K_{sp} is one example of a reaction equilibrium constant. Remember that, in the expression for K_{sp} , each concentration was raised to a power equal to its stoichiometric coefficient in the balanced chemical equation.

It is very interesting to compare this to the functional form of the equilibrium constant in Equation (9). The product NO_2 pressure appears in the numerator, and the exponent 2 on the pressure is the stoichiometric coefficient on NO_2 in the balanced chemical equation. The reactant N_2O_4 pressure appears in the denominator, and the exponent 1 on the pressure is the stoichiometric coefficient on N_2O_4 in the chemical equation. This is very similar to what we observed in solubility equilibrium, except that we now have the added factor of the reactant appearing in the denominator.

We now investigate whether other reactions have equilibrium constants and whether the form of this equilibrium constant is a happy coincidence or a general observation. We return to the reaction for the synthesis of ammonia, reaction (2):



In section II, we considered only the equilibrium produced when 1 mole of N_2 is reacted with 3 moles of H_2 . We now consider a range of possible initial values of these amounts, with the resultant equilibrium partial pressures given in Table 3. In addition, anticipating the possibility of an equilibrium constant, we have calculated the ratio of partial pressures given by Equation 10:

$$K_p = \frac{P(\text{NH}_3)^2}{P(\text{N}_2) \cdot P(\text{H}_2)^3}$$

In Table 3, the equilibrium partial pressures of the gases are in a very wide variety, including whether the final pressures are greater for reactants or products. However, from the data in Table 3, it is clear that, despite these variations, K_p in Equation (10) is essentially a constant for all of the initial conditions examined and is thus the “reaction equilibrium constant” for Reaction (2).

V(L)	n(N ₂)	n(H ₂)	P(N ₂)	P(H ₂)	P(NH ₃)	K _p
10	1	3	0.0342	0.1027	4.82	6.2·10 ⁵
10	0.1	0.3	0.0107	0.0322	0.467	6.0·10 ⁵
100	0.1	0.3	0.00323	0.00968	0.0425	6.1·10 ⁵
100	3	3	0.492	0.00880	0.483	6.1·10 ⁵
100	1	3	0.0107	0.0322	0.467	6.0·10 ⁵
1000	1.5	1.5	0.0255	0.00315	0.0223	6.2·10 ⁵

Equilibrium Partial Pressures of Reaction (2)

Studies of many chemical reactions of gases result in the same observations. Each reaction equilibrium can be described by an equilibrium constant in which the partial pressures of the products, each raised to their corresponding stoichiometric coefficient, are multiplied together in the numerator, and the partial pressures of the reactants, each raised to their corresponding stoichiometric coefficient, are multiplied together in the denominator. For historical reasons, this general observation is sometimes referred to as the “Law of Mass Action.”

Dynamic Equilibrium and Reaction Rates

Since we have studied rate laws for simple reactions, we should be able to use this information to understand the competition between the forward and reverse reactions, assuming both are elementary processes. Remember that an elementary process is a reaction which occurs in a single step. In the case of an elementary process, the rate law can be predicted from the coefficients in the reaction equation.

Let's apply this reasoning to the reaction in Equation (4), $\text{N}_2\text{O}_4(\text{g}) \rightarrow 2 \text{NO}_2(\text{g})$, where we determined the equilibrium constant in Equation (9). If the forward and reverse reactions are both elementary processes, then the rate laws for the forward and reverse reactions will be:

$$\text{Rate}_{\text{forward}} = k_{\text{forward}}[\text{N}_2\text{O}_4]$$

$$\text{Rate}_{\text{reverse}} = k_{\text{reverse}}[\text{NO}_2]^2$$

Assuming that the reaction comes to dynamic equilibrium, these two rates must be equal to each other. So let's set the right sides of the two equations equal to each other (and we'll let the subscript *f* stand for *forward* and the subscript *r* stand for *reverse*).

$$k_f[\text{N}_2\text{O}_4] = k_r[\text{NO}_2]^2$$

This is easily rearranged into a somewhat familiar form:

$$\frac{k_f}{k_r} = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]}$$

This looks very much like the equilibrium constant in Equation (9), except that this equation shows gas concentrations instead of gas pressures. We can use the Ideal Gas Law to make the connection, since for example $[\text{NO}_2] = n_{\text{NO}_2}/V = P_{\text{NO}_2}/RT$. If we substitute this into Equation (11), we get

$$\frac{k_f}{k_r} = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = \frac{P_{\text{NO}_2}^2}{P_{\text{N}_2\text{O}_4}} = \frac{1}{RT}$$

Just multiplying by RT , we can now see that

$$K_p = RT \frac{k_f}{k_r} = \frac{P_{\text{NO}_2}^2}{P_{\text{N}_2\text{O}_4}}$$

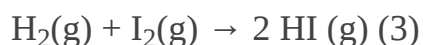
The equilibrium constant K_p is the ratio of the forward and reverse rate constants, times the factor RT . Equation (12) comes from two assumptions: that the reaction is in dynamic equilibrium, so that we can set the forward and reverse reaction rates

equal to each other, and that the forward and reverse reactions are elementary processes, so that we can write the rate laws easily. Since the result agrees with the experimental rate constant in Equation (9), we can conclude that these assumptions are valid. Therefore, the reaction equilibrium is a dynamic equilibrium, with equal forward and reverse reaction rates.

Although we demonstrated this outcome for a reaction in which the forward and reverse reactions are both elementary processes, it turns out that the result is general. This is trickier to show, but we can conclude that reactions in equilibrium are in dynamic equilibrium.

Observation 3: Temperature Dependence of the Reaction Equilibrium

We have previously observed that phase equilibrium, and in particular vapor pressure, depends on the temperature, but we have not yet studied the variation of reaction equilibrium with temperature. We focus our initial study on the reaction



and we measure the equilibrium partial pressures at a variety of temperatures. From these measurements, we can compile the data showing the temperature dependence of the equilibrium constant K_p for this reaction in Table 4.

Note that the equilibrium constant increases dramatically with temperature, more than tripling over this temperature range. As a result, at equilibrium, the pressure of HI must also increase dramatically as the temperature is increased.

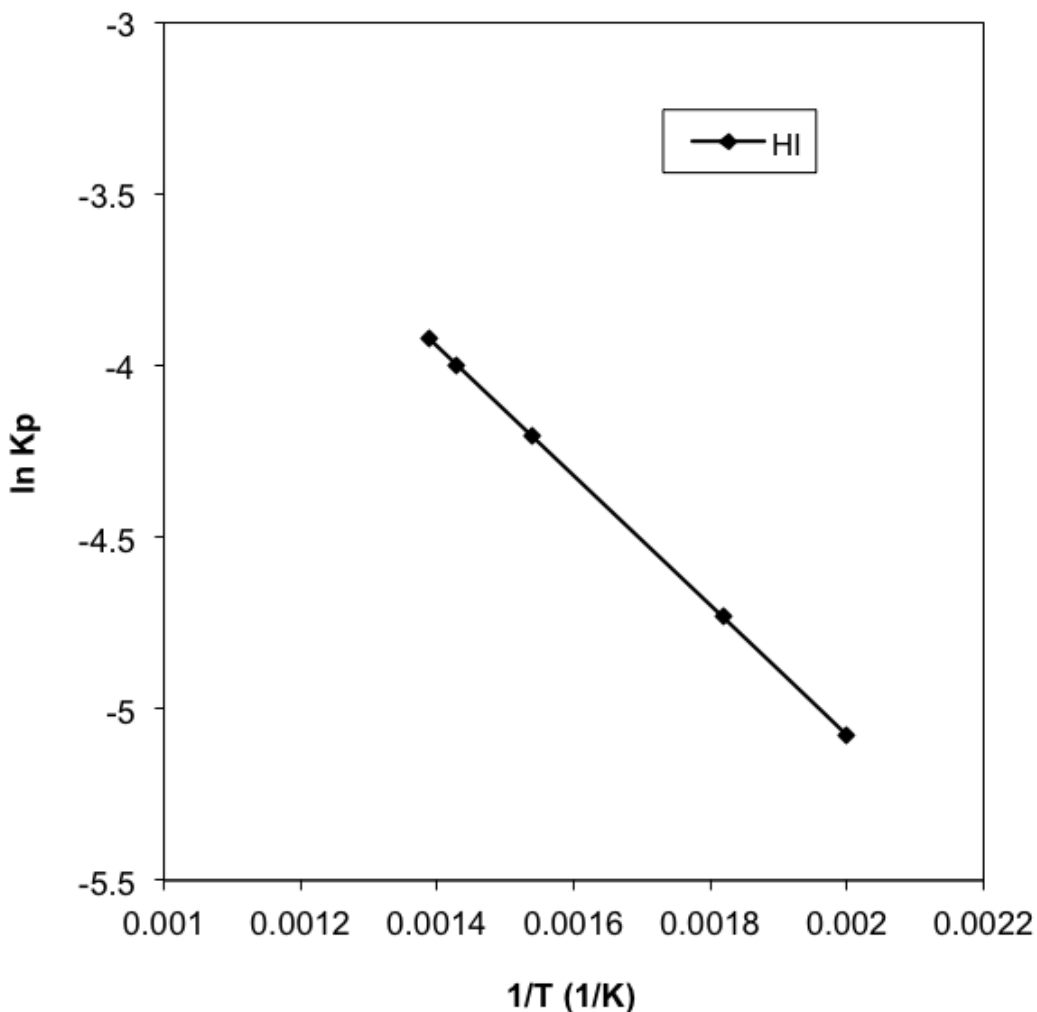
T(K)	K_p
500	$6.25 \cdot 10^{-3}$
550	$8.81 \cdot 10^{-3}$
650	$1.49 \cdot 10^{-2}$
700	$1.84 \cdot 10^{-2}$

These data do not seem to give a simple relationship between K_p and temperature. We must appeal to arguments based on Thermodynamics, which we will develop in a future Concept Development Study. From Thermodynamics, it is possible to show that the equilibrium constant should vary with temperature according to the following equation:

$$\ln K_p = \frac{-\Delta H^\circ}{RT} = \frac{\Delta S^\circ}{R}$$

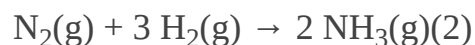
If ΔH° and ΔS° do not depend strongly on the temperature, then this equation would predict a simple straight line relationship between $\ln K_p$ and $1/T$. In addition, the slope of this line should be $-\Delta H^\circ/R$. We test this possibility with the graph in Figure 4.

Figure 4



In fact, we do observe a straight line through the data. In this case, the line has a negative slope. Note carefully that this means that K_p is *increasing* with temperature. The negative slope via Equation(14) means that $-\Delta H^\circ/R$ must be negative, and indeed for Reaction (3) in this temperature range, $\Delta H^\circ = 15.6$ kJ/mol. This value matches well with the slope of the line in Figure 4.

Given the validity of Equation (13) in describing the temperature dependence of the equilibrium constant, we should predict that an exothermic reaction with $\Delta H^\circ < 0$ should have a positive slope in the graph of $\ln K_p$ versus $1/T$. We thus predict that the equilibrium constant should *decrease* with increasing temperature. Let's test this. A good example of an exothermic reaction is Reaction (2)

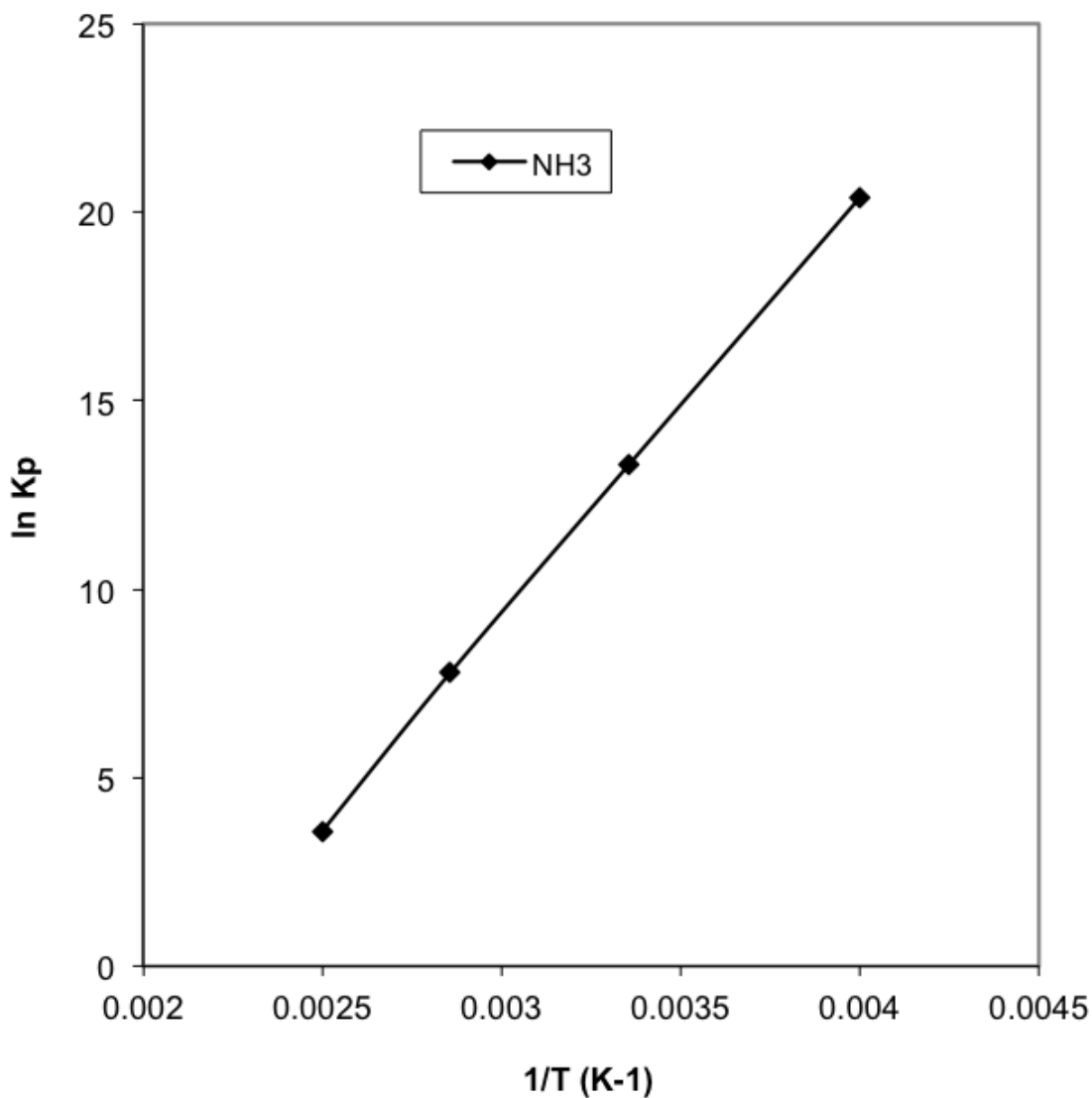


for which $\Delta H^\circ = -92.2 \text{ kJ/mol}$. Equilibrium constant data are given in Table 5. Note that, as predicted, the equilibrium constant for this exothermic reaction decreases rapidly with increasing temperature. The data from Table 5 is shown in Figure 5, clearly showing the contrast between the endothermic reaction and the exothermic reaction. The slope of the graph is positive for the exothermic reaction and negative for the endothermic reaction. From Equation (13), this is a general result for all reactions.

T(K)	K_p
250	$7 \cdot 10^8$
298	$6 \cdot 10^5$
350	$2 \cdot 10^3$
400	36

Equilibrium Constant for Reaction (2)

Figure 5



Observation 4: Changes in Equilibrium and Le Châtelier's Principle

One of our goals at the outset was to determine whether it is possible to control the equilibrium that occurs during a gas reaction. We might want to force a reaction to produce as much of the products as possible. In the alternative, if there are unwanted by-products of a reaction, we might want conditions that minimize the product. We have observed that the amount of product varies with the quantities of initial

materials and with changes in the temperature. Our goal is a systematic understanding of these variations.

A look back at Tables 1 and 2 shows that the equilibrium pressure of the product of the reaction increases with increasing the initial quantity of reaction. This seems quite intuitive. Less intuitive is the variation of the equilibrium pressure of the product of Reaction (2) with variation in the volume of the container, as shown in Table 3. Note that the pressure of NH_3 decreases by more than a factor of ten when the volume is increased by a factor of ten. This means that, at equilibrium, there are fewer moles of NH_3 produced when the reaction occurs in a larger volume.

To understand this effect, we rewrite the equilibrium constant in Equation (10) to explicitly show the volume of the container. This is done by applying Dalton's Law of partial pressures, so that each partial pressure is given by the Ideal Gas Law:

$$K_p = \frac{n(\text{NH}_3)^2 \left(\frac{RT}{V}\right)^2}{n(\text{N}_2) \left(\frac{RT}{V}\right) \cdot n(\text{H}_2)^3 \left(\frac{RT}{V}\right)^3} = \frac{n(\text{NH}_3)^2}{n(\text{N}_2) \cdot n(\text{H}_2)^3 \left(\frac{RT}{V}\right)^2}$$

Therefore,

$$K_p \left(\frac{RT}{V}\right)^2 = \frac{n(\text{NH}_3)^2}{n(\text{N}_2) \cdot n(\text{H}_2)^3}$$

This form of the equation makes it clear that, when the volume increases, the left side of the equation decreases. This means that the right side of the equation must decrease also, and in turn, $n(\text{NH}_3)$ must decrease while $n(\text{N}_2)$ and $n(\text{H}_2)$ must increase. The equilibrium is thus shifted from products to reactants when the volume increases for Reaction (2).

The effect of changing the volume must be considered for each specific reaction, because the effect depends on the stoichiometry of the reaction. One way to determine the consequence of a change in volume is to rewrite the equilibrium constant as we have done in Equation (15).

Finally, we consider changes in temperature. We note that K_p increases with T for endothermic reactions and decreases with T for exothermic reactions. As such, the products are increasingly favored with increasing temperature when the reaction is endothermic, and the reactants are increasingly favored with increasing temperature when the reaction is exothermic. On reflection, we note that when the reaction is exothermic, the reverse reaction is endothermic. Putting these statements together, we can say that the reaction equilibrium always shifts in the direction of the endothermic reaction when the temperature is increased.

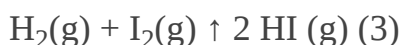
All of these observations can be collected into a single unifying concept known as Le Châtelier's principle. This principle can be stated as follows: when a reaction at equilibrium is stressed by a change in conditions, the equilibrium will be reestablished in such a way as to counter the stress. This statement is best understood by reflection on the types of "stresses" we have considered in this section. When a reactant is added to a system at equilibrium, the reaction responds by consuming some of that added reactant as it establishes a new equilibrium. This offsets some of the stress of the increase in reactant. When the temperature is raised for a reaction at equilibrium, this adds thermal energy. The system shifts the equilibrium in the endothermic direction, thus absorbing some of the added thermal energy, countering the stress.

The most challenging of the three types of stress considered in this section is the change in volume. By increasing the volume containing a gas phase reaction at equilibrium, we reduce the partial pressures of all gases present and thus reduce the total pressure. Recall that the response of Reaction (2) to the volume increase was to create more of the reactants at the expense of the products. One consequence of this shift is that more gas molecules are created, and this increases the total pressure in the reaction flask. Thus, the reaction responds to the stress of the volume increase by partially offsetting the pressure decrease with an increase in the number of moles of gas at equilibrium.

Le Châtelier's principle is a useful mnemonic for predicting how we might increase or decrease the amount of product at equilibrium by changing the conditions of the reaction. From this principle, we can predict whether the reaction should occur at high temperature or low temperature, and whether it should occur at high pressure or low pressure.

Review and Discussion Questions

1. In the data given for equilibrium of Reaction (3) on Page 3, there is no volume given. Show that changing the volume for Reaction (3) does not change the number of moles of reactants and products present at equilibrium, i.e. changing the volume does not shift the equilibrium.



2. For Reaction (4)



the number of moles of NO_2 at equilibrium increases if we increase the volume in which the reaction is contained. Explain why this must be true in terms of

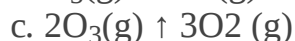
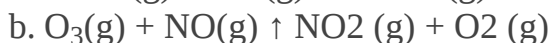
dynamic equilibrium, give a reason why the rates of the forward and reverse reactions might be affected differently by changes in the volume.

3. We could balance Reaction (2) by writing



Write the form of the equilibrium constant for the reaction balanced as in Reaction (2'). What is the value of the equilibrium constant? (Refer to Table 3.) Of course, the pressures at equilibrium do not depend on whether the reaction is balanced as in Reaction (2) or as in Reaction (2'). Explain why this is true, even though the equilibrium constant can be written differently and have a different value.

4. Show that the equilibrium constant K_p in Equation (10) for Reaction (2) can be written in terms of the concentrations or particle densities, e.g. $[\text{N}_2] = n_{\text{N}_2}/V$, instead of the partial pressures. In this form, we call the equilibrium constant K_c . Find the relationship between K_p and K_c , and calculate the value of K_c .
5. For each of these reactions, predict whether increases in temperature will shift the reaction equilibrium more towards products or more towards reactants.



6. Plot the data in Table 4 on a graph showing K_p on the y-axis and T on the x-axis. The shape of this graph is reminiscent of the graph of another physical property as a function of increasing temperature. Identify that property, and suggest a reason why the shapes of the graphs might be similar.
7. Using Le Châtelier's principle, predict whether the specified "stress" will produce an increase or a decrease in the amount of product observed at equilibrium for the reaction:



- a. Volume of container is increased.
b. Helium is added to container.
c. Temperature of container is raised.
d. Hydrogen is added to container.
e. CH_3OH is extracted from container as it is formed.

Acid Ionization Equilibrium

Foundation

We have developed an understanding of equilibrium involving phase transitions and involving reactions entirely in the gas phase. We will assume an understanding of the principles of dynamic equilibrium, reaction equilibrium constants, and Le Châtelier's principle. To understand the application of these principles to reactions in solution, we will now assume a definition of certain classes of substances as being either acids or bases. An acid is a substance whose molecules donate positive hydrogen ions (protons) to other molecules or ions. When dissolved in pure water, acid molecules will transfer a hydrogen ion to a water molecule or to a cluster of several water molecules. This increases the concentration of H^+ ions in the solution. A base is a substance whose molecules accept hydrogen ions from other molecules. When dissolved in pure water, base molecules will accept a hydrogen ion from a water molecule, leaving behind an increased concentration of OH^- ions in the solution. To understand what determines acid-base behavior, we will assume an understanding of the bonding, structure, and properties of individual molecules.

Goals

Acids and bases are very common substances whose properties vary greatly. Many acids are known to be quite corrosive, with the ability to dissolve solid metals or burn flesh. Many other acids, however, are not only benign but vital to the processes of life. Far from destroying biological molecules, they carry out reactions critical for organisms to live. Similarly, many bases are caustic cleansers while many others are medications to calm indigestion pains.

In this Concept Development Study, we will develop an understanding of the characteristics of molecules that make them either acids or bases. We will examine measurements about the relative strengths of acids and bases, and we will use these to develop a quantitative understanding of the relative strengths of acids and bases. From this, we can develop a qualitative understanding of the properties of molecules which determine whether a

molecule is a strong acid or a weak acid, a strong base or a weak base. This understanding is valuable in predicting the outcomes of reactions, based on the relative quantitative strengths of acids and bases. These reactions are commonly referred to as neutralization reactions. A surprisingly large number of reactions, particularly in organic chemistry, can be understood as transfer of hydrogen ions from acid molecules to base molecules.

Observation 1: Strong Acids and Weak Acids

From the definition of an acid given in the Foundation, a typical acid can be written as HA, representing the hydrogen ion which will be donated and the rest of the molecule which will remain as a negative ion after the donation. The typical reaction of an acid in an aqueous solution reacting with water can be written as



In this reaction, the hydronium ion $\text{H}_3\text{O}^+(\text{aq})$ is a notation to indicate that the donated proton has been dissolved in solution. However, experimental observations indicate that the proton is associated with several water molecules in a cluster, rather than attached to a single molecule. As such, H_3O^+ is a simplified notation to represent this result. Similarly, the $\text{A}^-(\text{aq})$ ion is solvated by several water molecules. Reaction (1) is referred to as "acid ionization."

Reaction (1) implies that a 0.1 M solution of the acid HA in water should produce H_3O^+ ions in solution with a concentration of 0.1 M. In fact, the concentration of H_3O^+ ions, $[\text{H}_3\text{O}^+]$, can be measured by a variety of techniques. Chemists commonly use a measure of the H_3O^+ ion concentration called the pH, defined by:

$$\text{pH} = -\log_{10}[\text{H}_3\text{O}^+]$$

We now observe the concentration $[\text{H}_3\text{O}^+]$ produced by dissolving a variety of acids in solution at a concentration of 0.1 M, and the results are tabulated in Table 1.

H ₂ SO ₄	0.1	1
HNO ₃	0.1	1
HCl	0.1	1
HBr	0.1	1
HI	0.1	1
HClO ₄	0.1	1
HClO ₃	0.1	1
HNO ₂	$6.2 \cdot 10^{-3}$	2.2
HCN	$7 \cdot 10^{-6}$	5.1
HIO	$1 \cdot 10^{-6}$	5.8
HF	$5.5 \cdot 10^{-3}$	2.3
HO-CN	$5.5 \cdot 10^{-3}$	2.3
HClO ₂	$2.8 \cdot 10^{-2}$	1.6
CH ₃ COOH (acetic acid)	$1.3 \cdot 10^{-3}$	2.9
CH ₃ CH ₂ COOH (propionic acid)	$1.1 \cdot 10^{-3}$	2.9

H₃O⁺, pH for 0.1 M acid solutions

Note that there are several acids listed for which [H₃O⁺] = 0.1 M, and pH = 1. This shows that, for these acids, the acid ionization is complete: essentially every acid molecule is ionized in the solution according to Reaction (1). However, there are other acids listed for which [H₃O⁺] is considerably less than 0.1 M and the pH is considerably greater than 1. For

each of these acids, therefore, not all of the acid molecules ionize according to Reaction (1). In fact, it is clear in Table 1 that in these acids the vast majority of the acid molecules do not ionize, and only a small percentage does ionize.

From these observations, we distinguish two classes of acids: "strong acids" and "weak acids." Strong acids are those for which nearly 100% of the acid molecules ionize, whereas weak acids are those for which only a small percentage of molecules ionize. There are seven strong acids listed in Table 1. From many observations, it is possible to determine that these seven acids are the only commonly observed strong acids. Otherwise, the vast majority of all substances with acidic properties are weak acids. We seek to characterize weak acid ionization quantitatively and to determine what the differences in molecular properties are between strong acids and weak acids.

Observation 2: Percent Ionization in Weak Acids

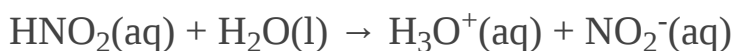
Table 1 shows that the pH of 0.1 M acid solutions varies from one weak acid to another. If we dissolve 0.1 moles of acid in a 1.0 L solution, the fraction of those acid molecules that will ionize varies from weak acid to weak acid. For a few weak acids, using the data in Table 1 we can calculate the percentage of ionized acid molecules in 0.1 M acid solutions in Table 2.

HNO ₂	$6.2 \cdot 10^{-3}$	6.2%
HCN	$7 \cdot 10^{-6}$	0.007%
HIO	$1 \cdot 10^{-6}$	0.001%
HF	$5.5 \cdot 10^{-3}$	5.5%

HOCN	$5.5 \cdot 10^{-3}$	5.5%
HClO ₂	$2.8 \cdot 10^{-2}$	28.2%
CH ₃ COOH (acetic acid)	$1.3 \cdot 10^{-3}$	1.3%
CH ₃ CH ₂ COOH (propionic acid)	$1.1 \cdot 10^{-3}$	1.1%

Percent Ionization of 0.1M acid solutions

We might be tempted to conclude from Table 2 that we can characterize the strength of each acid by the percent ionization of acid molecules in solution. However, before doing so, we observe the pH of a single acid, nitrous acid (HNO₂), in solution as a function of the concentration of the acid.



In this case, the "concentration of the acid" refers to the number of moles of acid that we dissolved per liter of water. Our observations are listed in Table 3, which gives [H₃O⁺], pH, and percent ionization as a function of nitrous acid concentration.

0.50	$1.7 \cdot 10^{-2}$	1.8	3.3%
0.20	$1.0 \cdot 10^{-2}$	2.0	5.1%
0.10	$7.0 \cdot 10^{-3}$	2.2	7.0%
0.050	$4.8 \cdot 10^{-3}$	2.3	9.7%
0.020	$2.9 \cdot 10^{-3}$	2.5	14.7%
0.010	$2.0 \cdot 10^{-3}$	2.7	20.0%

0.005	$1.3 \cdot 10^{-3}$	2.9	26.7%
0.001	$4.9 \cdot 10^{-4}$	3.3	49.1%
0.0005	$3.0 \cdot 10^{-4}$	3.5	60.8%

% Ionization of Nitrous Acid

Surprisingly, perhaps, the percent ionization varies considerably as a function of the concentration of the nitrous acid. We recall that this means that the fraction of molecules which ionize, according to Reaction (2), depends on how many acid molecules there are per liter of solution. Since some but not all of the acid molecules are ionized, this means that nitrous acid molecules are present in solution at the same time as the negative nitrite ions and the positive hydrogen ions. Recalling our observation of equilibrium in gas phase reactions, we can conclude that Reaction (2) achieves equilibrium for each concentration of the nitrous acid.

Since we know that gas phase reactions come to equilibrium under conditions determined by the equilibrium constant, we might speculate that the same is true of reactions in aqueous solution, including acid ionization. We therefore define an analogy to the gas phase reaction equilibrium constant. In this case, we would not be interested in the pressures of the components, since the reactants and products are all in solution. Instead, we try a function composed of the equilibrium concentrations:

$$K = \frac{[\text{H}_3\text{O}^+][\text{NO}_2^-]}{[\text{HNO}_2][\text{H}_2\text{O}]}$$

The concentrations at equilibrium can be calculated from the data in Table 3 for nitrous acid. $[\text{H}_3\text{O}^+]$ is listed and $[\text{NO}_2^-] = [\text{H}_3\text{O}^+]$. Furthermore, if c_0 is the initial concentration of the acid defined by the number of moles of acid dissolved in solution per liter of solution, then $[\text{HA}] = c_0 - [\text{H}_3\text{O}^+]$. Note that the contribution of $[\text{H}_2\text{O}(l)]$ to the value of the function K is simply a constant. This is because the "concentration" of water in the solution is simply the molar density of water, $n_{\text{H}_2\text{O}}/V = 55.5 \text{ M}$, which is not affected by the presence or absence of solute. All of the relevant concentrations,

along with the function in Equation (3) are calculated and tabulated in Table 4:

0.50	$1.7 \cdot 10^{-2}$	$1.7 \cdot 10^{-2}$	0.48	$1.0 \cdot 10^{-5}$
0.20	$1.0 \cdot 10^{-2}$	$1.0 \cdot 10^{-2}$	0.19	$9.9 \cdot 10^{-6}$
0.10	$7.0 \cdot 10^{-3}$	$7.0 \cdot 10^{-3}$	$9.3 \cdot 10^{-2}$	$9.6 \cdot 10^{-6}$
0.050	$4.8 \cdot 10^{-3}$	$4.8 \cdot 10^{-3}$	$4.5 \cdot 10^{-2}$	$9.4 \cdot 10^{-6}$
0.020	$2.9 \cdot 10^{-3}$	$2.9 \cdot 10^{-3}$	$1.7 \cdot 10^{-2}$	$9.1 \cdot 10^{-6}$
0.010	$2.0 \cdot 10^{-3}$	$2.0 \cdot 10^{-3}$	$8.0 \cdot 10^{-3}$	$8.9 \cdot 10^{-6}$
0.005	$1.3 \cdot 10^{-3}$	$1.3 \cdot 10^{-3}$	$3.6 \cdot 10^{-3}$	$8.8 \cdot 10^{-6}$
0.001	$4.9 \cdot 10^{-4}$	$4.9 \cdot 10^{-4}$	$5.1 \cdot 10^{-4}$	$8.5 \cdot 10^{-6}$
0.0005	$3.0 \cdot 10^{-4}$	$3.0 \cdot 10^{-4}$	$2.0 \cdot 10^{-4}$	$8.5 \cdot 10^{-6}$

Equilibrium Concentrations and K for Nitrous Acid

We note that the function K in Equation (3) is approximately, though only approximately, the same for all conditions analyzed in Table 3. Variation of the concentration by a factor of 1000 produces a change in K of only 10-15%. Hence, we can regard the function K as a constant which approximately describes the acid ionization equilibrium for nitrous acid. By convention, chemists omit the constant concentration of water from the equilibrium expression, resulting in the acid ionization equilibrium constant, K_a , defined as:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{NO}_2^-]}{[\text{HNO}_2]}$$

From an average of the data in Table 4, we can calculate that, at 25 °C for nitrous acid, $K_a = 5 \cdot 10^{-4}$. Acid ionization constants for the other weak acids in Table 2 are listed in Table 5.

HNO ₂	$5 \cdot 10^{-4}$	3.3
HCN	$4.9 \cdot 10^{-10}$	9.3
HIO	$2.3 \cdot 10^{-11}$	10.6
HF	$3.5 \cdot 10^{-4}$	3.4
HOCN	$3.5 \cdot 10^{-4}$	3.4
HClO ₂	$1.1 \cdot 10^{-2}$	2.0
CH ₃ COOH (acetic acid)	$1.7 \cdot 10^{-5}$	4.8
CH ₃ CH ₂ COOH (propionic acid)	$1.4 \cdot 10^{-5}$	4.9

Weak Acid Ionization Constants, K

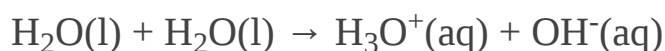
We make two final notes about the results in Table 5. First, it is clear the larger the value of K_a , the stronger the acid. That is, when K_a is a larger number, the percent ionization of the acid is larger, and vice versa. Second, the values of K_a vary over many orders of magnitude. As such, it is often convenient to define the quantity $\text{p}K_a$, analogous to pH, for purposes of comparing acid strengths:

$$\text{p}K_a = -\log_{10} K_a$$

The value of pK_a for each acid is also listed in Table 5. Note that a small value of pK_a implies a large value of K_a and thus a stronger acid. Weaker acids have larger values of pK_a . K_a and pK_a thus give a simple quantitative comparison of the strength of weak acids.

Observation 3: Autoionization of Water

Since we have the ability to measure pH for acid solutions, we can measure pH for pure water as well. It might seem that this would make no sense, as we would expect $[H_3O^+]$ to equal zero exactly in pure water. Surprisingly, this is incorrect: a measurement on pure water at 25 °C yields $pH = 7$, so that $[H_3O^+] = 1.0 \cdot 10^{-7}$ M. There can be only one possible source for these ions: water molecules. The process



is referred to as the "autoionization" of water. Note that, in this reaction, some water molecules behave as acid, donating protons, while other acid molecules behave as base, accepting protons.

Since at equilibrium $[H_3O^+] = 1.0 \cdot 10^{-7}$ M, it must also be true that $[OH^-] = 1.0 \cdot 10^{-7}$ M. We can write the equilibrium constant for Reaction (6), following our previous convention of omitting the pure water from the expression, and we find that, at 25 °C,

$$K_w = [H_3O^+][OH^-] = 1.0 \cdot 10^{-14}$$

(In this case, the subscript "w" refers to "water.")

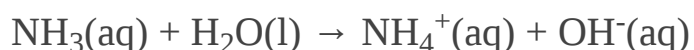
Reaction (6) occurs in pure water but must also occur when ions are dissolved in aqueous solutions. This includes the presence of acids ionized in solution. For example, we consider a solution of 0.1 M acetic acid. Measurements show that in this solution, $[H_3O^+] = 1.3 \cdot 10^{-3}$ M and $[OH^-] = 7.7 \cdot 10^{-12}$ M. We note two things from this observation: first, the value of $[OH^-]$ is considerably less than in pure water; second, the autoionization equilibrium constant remains the same at $1.0 \cdot 10^{-14}$. From these notes, we can conclude that the autoionization equilibrium of water occurs in acid

solution, but the extent of autoionization is suppressed by the presence of the acid in solution.

We consider a final note on the autoionization of water. The pH of pure water is 7 at 25 °C. Adding any acid to pure water, no matter how weak the acid, must increase $[\text{H}_3\text{O}^+]$, thus producing a pH below 7. As such, we can conclude that, for all acid solutions at 25 °C, their pH is less than 7, or in other words, any solution with pH less than 7 is acidic.

Observation 4: Base Ionization, Neutralization and Hydrolysis of Salts

We have not yet examined the behavior of base molecules in solution, nor have we compared the relative strengths of bases. We have defined a base molecule as one which accepts a positive hydrogen ion from another molecule. One of the most common examples is ammonia, NH_3 . When ammonia is dissolved in aqueous solution, the following reaction occurs:



Due to the lone pair of electrons on the highly electronegative N atom, NH_3 molecules will readily attach a free hydrogen ion forming the ammonium ion NH_4^+ . When we measure the concentration of OH^- for various initial concentration of NH_3 in water, we observe the results in Table 6. We should anticipate that a base ionization equilibrium constant might exist comparable to the acid ionization equilibrium constant, and in Table 6, we have also calculated the value of the function K_b defined as:

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$

0.50	$3.2 \cdot 10^{-3}$	$2.0 \cdot 10^{-5}$	11.5
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0.20	$2.0 \cdot 10^{-3}$	$2.0 \cdot 10^{-5}$	11.3
0.10	$1.4 \cdot 10^{-3}$	$2.0 \cdot 10^{-5}$	11.1
0.050	$9.7 \cdot 10^{-4}$	$1.9 \cdot 10^{-5}$	11.0
0.020	$6.0 \cdot 10^{-4}$	$1.9 \cdot 10^{-5}$	10.8
0.010	$4.2 \cdot 10^{-4}$	$1.9 \cdot 10^{-5}$	10.6
0.005	$3.0 \cdot 10^{-4}$	$1.9 \cdot 10^{-5}$	10.5
0.001	$1.3 \cdot 10^{-4}$	$1.8 \cdot 10^{-5}$	10.1
0.0005	$8.7 \cdot 10^{-5}$	$1.8 \cdot 10^{-5}$	9.9

Equilibrium Concentrations and K_b for Ammonia

Given that we have dissolved a base in pure water, we might be surprised to discover the presence of positive hydronium ions, H_3O^+ , in solution, but a measurement of the pH for each of the solutions reveals small amounts. The pH for each solution is also listed in Table 6. The source of these H_3O^+ ions must be the autoionization of water. Note, however, that in each case in basic solution, the concentration of H_3O^+ ions is less than that in pure water. Hence, the presence of the base in solution has suppressed the autoionization. Because of this, in each case the pH of a basic solution is greater than 7.

Base ionization is therefore quite analogous to acid ionization observed earlier. We now consider a comparison of the strength of an acid to the strength of a base. To do so, we consider a class of reactions called "neutralization reactions," which occur when we mix an acid solution with a base solution. Since the acid donates protons and the base accepts protons, we might expect, when mixing acid and base, to achieve a solution which is no longer acidic or basic. For example, if we mix together equal volumes of 0.1 M $HCl(aq)$ and 0.1 M $NaOH(aq)$, the following reaction occurs:



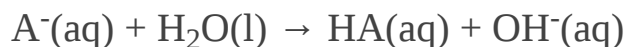
The resultant solution is simply a salt solution with NaCl dissolved in water. This solution has neither acidic nor basic properties, and the pH is 7; hence the acid and base have neutralized each other. In this case, we have mixed together a strong acid with a strong base. Since both are strong and since we mixed equal molar quantities of each, the neutralization reaction is essentially complete.

We next consider mixing together a weak acid solution with a strong base solution, again with equal molar quantities of acid and base. As an example, we mix 100 mL of 0.1 M acetic acid (CH_3COOH) solution with 100 mL of 0.1 M sodium hydroxide. In this discussion, we will abbreviate the acetic acid molecular formula CH_3COOH as HA and the acetate ion CH_3COO^- as A^- . The reaction of HA and NaOH is:



$\text{A}^-(\text{aq})$ is the acetate ion in solution, formed when an acetic acid molecule donates the positive hydrogen ion. We have thus created a salt solution again, in this case of sodium acetate in water. Note that the volume of the combined solution is 200 mL, so the concentration of sodium acetate (NaA) in solution is 0.050 M.

Unlike our previous NaCl salt solution, a measurement in this case reveals that the pH of the product salt solution is 9.4, indicating that the solution is basic. Thus, mixing equal molar quantities of strong base with weak acid produces a basic solution. In essence, the weak acid does not fully neutralize the strong base. To understand this, we examine the behavior of sodium acetate in solution. Since the pH is greater than 7, then there is an excess of OH^- ions in solution relative to pure water. These ions must have come from the reaction of sodium acetate with the water. Therefore, the negative acetate ions in solution must behave as a base, accepting positive hydrogen ions:



The reaction of an ion with water to form either an acid or a base solution is referred to as "hydrolysis." From this example, the salt of a weak acid behaves as a base in water, resulting in a pH greater than 7.

To understand the extent to which the hydrolysis of the negative ion occurs, we need to know the equilibrium constant for this reaction. This turns out to be determined by the acid ionization constant for HA. To see this, we write the equilibrium constant for the hydrolysis of A^- as

$$K_h = \frac{[HA][OH^-]}{[A^-]}$$

Multiplying numerator and denominator by $[H_3O^+]$, we find that

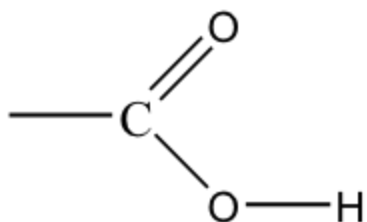
$$K_h = \frac{[HA][OH^-]}{[A^-]} \frac{[H_3O^+]}{[H_3O^+]} = \frac{[K_w]}{[K_a]}$$

Therefore, for the hydrolysis of acetate ions in solution, $K_h = 5.8 \cdot 10^{-10}$. This is fairly small, so the acetate ion is a very weak base.

Observation 5: Acid strength and molecular properties

We now have a fairly complete quantitative description of acid-base equilibrium. To complete our understanding of acid-base equilibrium, we need a predictive model which relates acid strength or base strength to molecular properties. In general, we expect that the strength of an acid is related either to the relative ease by which it can donate a hydrogen ion or by the relative stability of the remaining negative ion formed after the departure of the hydrogen ion.

To begin, we note that there are three basic categories of acids that we have examined in this study. First, there are simple binary acids: HF, HCl, HBr, and HI. Second, there are acids formed from main group elements combined with one or more oxygen atoms, such H_2SO_4 or HNO_3 . These are called "oxyacids." Third, there are the "carboxylic acids," organic molecules which contain the carboxylic functional group:



We consider first the simple binary acids. HCl, HBr, and HI are all strong acids, whereas HF is a weak acid. In comparing the experimental values of pK_a values in Table 7, we note that the acid strength increases in the order $HF < HCl < HBr < HI$. This means that the hydrogen ion can more readily separate from the covalent bond with the halogen atom (X) as we move down the periodic table. This is reasonable, because the strength of the H-X bond also decreases as we move down the periodic table, as shown in Table 7:

HF	3.1	567.7
HCl	-6.0	431.6
HBr	-9.0	365.9
HI	-9.5	298.0

H-X Bond Strengths and pK

The decreasing strength of the H-X bond is primarily due to the increase in the size of the X atom as we move down the periodic table. We conclude that one factor which influences acidity is the strength of the H-X bond: a weaker bond produces a stronger acid, and vice versa.

In the acids of the other two categories, the hydrogen atom that ionizes is attached directly to an oxygen atom. Thus, to understand acidity in these molecules, we must examine what the oxygen atom is in turn bonded to. It

is very interesting to note that, in examining compounds like R-O-H, where R is an atom or group of atoms, we can get either acidic or basic properties. As examples, NaOH is a strong base, whereas HOCl is a weak acid. This means that, when NaOH ionizes in solution, the Na-O linkage ionizes, whereas when HOCl ionizes in solution, the H-O bond ionizes.

To understand this behavior, we compare the strength of the simple oxyacids HOI, HOBr, and HOCl. The pK_a s for these acids are found experimentally to be, respectively, 10.6, 8.6, and 7.5. The acid strength for HOX increases as we move up the periodic table in the halogen group. This means that the H-O bond ionizes more readily when the oxygen atom is bonded to a more electronegative atom.

We can add to this observation by comparing the strengths of the acids HOCl, HOClO, HOClO₂, and HOClO₃. (Note that the molecular formulae are more commonly written as HClO, HClO₂, HClO₃, and HClO₄. We have written them instead to emphasize the molecular structure.) The pK_a 's of these acids are, respectively, 7.5, 2.0, -2.7, and -8.0. In each case, the molecule with more oxygen atoms on the central Cl atom is the stronger acid: HOClO is more acidic than HOCl, etc. A similar result is found in comparing the oxyacids of nitrogen. HONO₂, nitric acid, is one of the strong acids, whereas HONO, nitrous acid, is a weak acid. Since oxygen atoms are very strongly electronegative, these trends add to our observation that increasing the electronegativity of the attached atoms increases the ionization of the O-H bond.

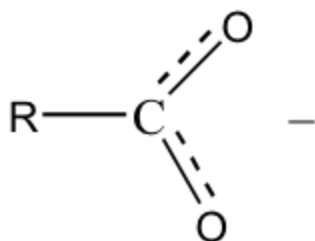
Why would electronegativity play a role in acid strength? There are two conclusions we might draw. First, a greater electronegativity of the atom or atoms attached to the H-O in the oxyacid apparently results in a weaker H-O bond, which is thus more readily ionized. We know that an electronegative atom polarizes bonds by drawing the electrons in the molecule towards it. In this case, the Cl in HOCl and the Br in HOBr must polarize the H-O bond, weakening it and facilitating the ionization of the hydrogen. In comparing HOCl to HOClO, the added oxygen atom must increase the polarization of the H-O bond, thus weakening the bond further and increasing the extent of ionization.

A second conclusion has to do with the ion created by the acid ionization. The negative ion produced has a surplus electron, and the relative energy of this ion will depend on how readily that extra electron is attracted to the atoms of the ion. The more electronegative those atoms are, the stronger is the attraction. Therefore, the OCl^- ion can more readily accommodate the negative charge than can the OBr^- ion. And the OCIO^- ion can more readily accommodate the negative charge than can the OCl^- ion.

We conclude that the presence of strongly electronegative atoms in an oxyacid increases the polarization of the H-O bond, thus facilitating ionization of the acid, and increases the attraction of the extra electron to the negative ion, thus stabilizing the negative ion. Both of these factors increase the acid strength. Chemists commonly use both of these conclusions in understanding and predicting relative acid strength.

The relative acidity of carbon compounds is a major subject of organic chemistry, which we can only visit briefly here. In each of the carboxylic acids, the H-O group is attached to a carbonyl $\text{C}=\text{O}$ group, which is in turn bonded to other atoms. The comparison we observe here is between carboxylic acid molecules, denoted as RCOOH , and other organic molecules containing the H-O group, such as alcohols denoted as ROH . (R is simply an atom or group of atoms attached to the functional group.) The former are obviously acids whereas the latter group contains molecules which are generally extremely weak acids. One interesting comparison is for the acid and alcohol when R is the benzene ring, C_6H_5 . Benzoic acid, $\text{C}_6\text{H}_5\text{COOH}$, has $\text{pK}_\text{a} = 4.2$, whereas phenol, $\text{C}_6\text{H}_5\text{OH}$, has $\text{pK}_\text{a} = 9.9$. Thus, the presence of the doubly bonded oxygen atom on the carbon atom adjacent to the O-H clearly increases the acidity of the molecule, and thus increases ionization of the O-H bond.

This observation is quite reasonable in the context of our previous conclusion. Adding an electronegative oxygen atom in near proximity to the O-H bond both increases the polarization of the O-H bond and stabilizes the negative ion produced by the acid ionization. In addition to the electronegativity effect, carboxylate anions, RCOO^- , exhibit resonance stabilization:



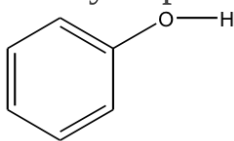
The resonance results in a sharing of the negative charge over several atoms, thus stabilizing the negative ion. This is a major contributing factor in the acidity of carboxylic acids versus alcohols.

Review and Discussion Questions

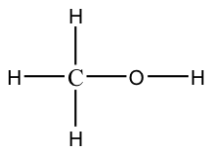
1. Strong acids have a higher percent ionization than do weak acids. Why don't we use percent ionization as a measure of acid strength, rather than K_a ?
2. Using the data in Table 4 for nitrous acid, plot $[H_3O^+]$ versus c_0 , the initial concentration of the acid, and versus $[HNO_2]$ the equilibrium concentration of the acid. On a second graph, plot $[H_3O^+]^2$ versus c_0 , the initial concentration of the acid, and versus $[HNO_2]$ the equilibrium concentration of the acid. Which of these results gives a straight line? Using the equilibrium constant expression, explain your answer.
3. Using Le Châtelier's principle, explain why the concentration of $[OH^-]$ is much lower in acidic solution than it is in neutral solution.
4. We considered mixing a strong base with a weak acid, but we did not consider mixing a strong acid with a weak acid. Consider mixing 0.1M HNO_3 and 0.1M HNO_2 . Predict the pH of the solution and the percent ionization of the nitrous acid. Rationalize your prediction using Le Châtelier's principle.
5. Imagine taking a 0.5M solution of nitrous acid and slowly adding water to it. Looking at Table 3, we see that, as the concentration of nitrous acid decreases, the percent ionization increases. By contrast, $[H_3O^+]$ decreases. Rationalize these results using Le Châtelier's principle.
6. We observed that mixing a strong acid and a strong base, in equal amounts and concentrations, produces a neutral solution, and that mixing a strong base with a weak acid, in equal amounts and

concentrations, produces a basic solution. Imagine mixing a weak acid and a weak base, in equal amounts and concentrations. Predict whether the resulting solution will be acidic, basic, or neutral, and explain your prediction.

7. Using the electronegativity arguments presented in Section VII, explain why, in general, compounds like M-O-H are bases rather than acids, when M is a metal atom. Predict the relationship between the properties of the metal atom M and the strength of the base MOH.
8. Ionization of sulfuric acid H_2SO_4 produces HSO_4^- , which is also an acid. However, HSO_4^- is a much weaker acid than H_2SO_4 . Using the conclusions from Section VII, explain why HSO_4^- is a much weaker acid.
9. Predict and explain the relative acid strengths of H_2S and HCl . Predict and explain the relative acid strengths of H_3PO_4 and H_3AsO_4 .
10. Using arguments from Section VII, predict and explain the relative acidity of phenol and methanol:



Phenol



Methanol

Entropy and the Second Law of Thermodynamics

Introduction

We have spent much of the previous concept studies finding that chemical and physical processes come to equilibrium. We have observed this in phase equilibrium of pure substances, solution equilibrium, solubility equilibrium, chemical reactions in the gas phase, and acid-base equilibrium. In each case, we have been able to understand equilibrium as a dynamic process. At equilibrium, there are competing processes, forward and reverse, which come to equilibrium when the rates of the competing processes are equal. For example, when liquid and vapor are at equilibrium at the vapor pressure of the liquid, the rate of evaporation of the liquid is equal to the rate of condensation of the vapor.

However, our dynamic equilibrium model does not tell us the conditions at equilibrium. For each liquid, we know that there is one pressure for each temperature at which the liquid can be in equilibrium with its vapor. But we cannot predict or calculate what that pressure is for each temperature for each liquid. We can only make qualitative predictions. Thermodynamics will give us the means to make these predictions and will give us a new physical insight into the nature of equilibrium.

We will begin by developing a means to predict what processes will happen “spontaneously.” This is a term chemists use to refer to processes that are not at equilibrium. It is easiest to explain with an example. We know that, if the pressure of water vapor is 1 atm at 25 °C, the water vapor will spontaneously condense. On the other hand, we have also seen that, if the pressure of water vapor is below 23 torr at 25 °C, the liquid water will spontaneously evaporate. These are both examples of spontaneous processes. Note that these are opposite processes. This means that the spontaneity of a process depends on the conditions, in this case, the pressure and the temperature. Any process not at equilibrium is a process occurring spontaneously. One way to understand equilibrium, then, is to understand spontaneity. We will see that the Second Law of Thermodynamics provides us the ability to predict spontaneous processes.

Foundation

We have come a long way to reach this point, so we have a substantial foundation to build on. We know all the elements of the Atomic Molecular Theory, including the models for molecular structure and bonding. We have developed the postulates of the Kinetic Molecular Theory. We have observed and defined phase transitions and phase equilibrium. We have also observed equilibrium in a variety of reaction systems, including acids and bases. We will assume an understanding of the energetics of chemical reactions, including the idea of a “state function” and the concept of Hess’ Law.

Observation 1: Spontaneous Mixing

We begin by examining common characteristics of spontaneous processes, and for simplicity, we focus on processes not involving phase transitions or chemical reactions. A very clear example of such a process is mixing. Imagine adding a drop of blue ink into a glass of water. At first, the blue dye in the ink is highly concentrated. Therefore, the molecules of the dye are closely congregated. Slowly but steadily, the dye begins to diffuse throughout the entire glass of water, so that eventually the water appears as a uniform blue color. This occurs more readily with agitation or stirring but occurs spontaneously even without such effort. Careful measurements show that this process occurs without a change in temperature, so there is no energy input or released during the mixing.

We conclude that, although there is no energetic advantage to the dye molecules dispersing themselves, they do so spontaneously. Furthermore, this process is “irreversible” in the sense that, without considerable effort on our part, the dye molecules will never return to form a single localized drop. We now seek an understanding of how and why this mixing occurs.

Consider the following rather abstract model for the dye molecules in the water. For the glass, we take a row of 10 small boxes, each one of which represents a possible location for a molecule, either of water or of dye. For the molecules, we take marbles, colorless for water and blue for ink. Each box will accommodate only a single marble, since two molecules cannot be

in the same place as the same time. Since we see a drop of dye when the molecules are congregated, we model a "drop" as three blue marbles in consecutive boxes. Notice that there are only eight ways to have a "drop" of dye, assuming that the three dye "molecules" are indistinguishable from one another. Two possibilities are shown in Figures 1a and 1b. It is not difficult to find the other six.

By contrast, there are many more ways to arrange the dye molecules so that they do not form a drop, i.e., so that the three molecules are not together. Two possibilities are shown in Figures 1c and 1d. The total number of such possibilities is 112. (The total number of all possible arrangements can be calculated as follows: there are 10 possible locations for the first blue marble, 9 for the second, and 8 for the third. This gives 720 possible arrangements, but many of these are identical, since the marbles are indistinguishable. The number of duplicates for each arrangement is 6, calculated from three choices for the first marble, two for the second, and one for the third. The total number of non-identical arrangements of the molecules is $720/6 = 120$.) We conclude that, if we randomly place the 3 marbles in the tray of 10 boxes, the chances are only 8 out of 120 (or 1 out of 15) of observing a drop of ink.

Figure 1
Arrangements of Three Ink Molecules

(a) an unmixed state



(b) another unmixed state



(c) a mixed state



(d) another mixed state



Now, in a real experiment, there are many, many times more ink molecules and many, many times more possible positions for each molecule. To see how this comes into play, consider a row of 500 boxes and 5 blue marbles. (The "mole fraction" of ink is thus 0.01.) The total number of distinct configurations of the blue marbles in these boxes is approximately 2×10^{11} . The number of these configurations that have all five ink marbles together in a drop is 496. If the arrangements are sampled randomly, the chances of observing a drop of ink with all five molecules together are thus approximately one in 500 million. The possibilities are remote even for observing a partial "droplet" consisting of fewer than all five dye molecules. The chance for four of the molecules to be found together is about one in 800,000. Even if we define a droplet to be only three molecules together, the chances of observing one are less than one in 1600.

We could, with some difficulty, calculate the probability for observing a drop of ink when there are 10^{23} molecules. However, we can reasonably extrapolate from our small calculations that the probability is essentially zero for the ink molecules, randomly distributed into the water molecules, to be found together. The reason why we observe ink to disperse in water is that the probability is infinitesimally small for randomly distributed dye molecules to be congregated in a drop.

Interestingly, however, when we set up the real ink and water experiment, we did not randomly distribute the ink molecules. Rather, we began initially with a drop of ink in which the dye molecules were already congregated. We know that, according to the Kinetic Molecular Theory, the molecules are in constant random motion. Therefore, they must be constantly rearranging themselves. Since these random motions do not energetically favor any one arrangement over any other one arrangement, we can assume that all possible arrangements are equally probable. Since most of the arrangements do not correspond to a drop of ink, then most of the time we will not observe a drop. In the case above with five blue marbles in 500 boxes, we expect to see a drop only once in every 500 million times we look at the "glass." In a real glass of water with a real drop of ink, the chances are very much smaller than this.

We draw two very important conclusions from our model. First, the random motions of molecules make every possible arrangement of these molecules equally probable. Second, mixing occurs spontaneously simply because there are vastly many more arrangements which are mixed than which are not. The first conclusion tells us "how" mixing occurs, and the second tells us "why." On the basis of these observations, we deduce the following preliminary generalization: a spontaneous process occurs because it produces the most probable final state.

Probability and Entropy

There is a subtlety in our conclusion to be considered in more detail. We have concluded that all possible arrangements of molecules are equally probable. We have further concluded that mixing occurs because the final mixed state is overwhelmingly probable. Placed together, these statements appear to be openly contradictory. To see why they are not, we must analyze the statements carefully. By an "arrangement" of the molecules, we mean a specification of the location of each and every molecule. We have assumed that, due to random molecular motion, each such arrangement is equally probable. In what sense, then, is the final state "overwhelmingly probable"?

Recall the system illustrated in Figure 1, where we placed three identical blue marbles into ten spaces. We calculated before that there are 120 unique ways to do this. If we ask for the probability of the arrangement in Figure 1a, the answer is thus $1/120$. This is also the probability for each of the other possible arrangements, according to our model. However, if we now ask instead for the probability of observing a "mixed" state (with no drop), the answer is $112/120$, whereas the probability of observing an "unmixed" state (with a drop) is only $8/120$. Clearly, the probabilities are not the same when considering the less specific characteristics "mixed" and "unmixed."

In Chemistry we are virtually never concerned with "microscopic" details, such as the locations of specific individual molecules. Rather, we are interested in more general characteristics, such as whether a system is mixed or not, or what the temperature or pressure is. These properties of interest to us are "macroscopic." As such, we refer to a specific arrangement

of the molecules as a "microstate," and each general state (mixed or unmixed, for example) as a "macrostate." All microstates have the same probability of occurring, according to our model. As such, the macrostates have widely differing probabilities.

We come to an important result: the probability of observing a particular macrostate (e.g., a mixed state) is proportional to the number of microstates with that macroscopic property. For example, from Figure 1, there are 112 arrangements (microstates) with the "mixed" macroscopic property. As we have discussed, the probability of observing a mixed state is 112/120, which is obviously proportional to 112. Thus, one way to measure the relative probability of a particular macrostate is by the number of microstates W corresponding to that macrostate. W stands for "ways", i.e. there are 112 "ways" to get a mixed state in Figure 1.

Now we recall our conclusion that a spontaneous process always produces the outcome with greatest probability. Since W measures this probability for any substance or system of interest, we could predict using W whether the process leading from a given initial state to a given final state was spontaneous by simply comparing probabilities for the initial and final states. For reasons described below, we instead define a function of W ,

$$S(W) = k \ln W ,$$

called the "entropy," which can be used to make such predictions about spontaneity. (The " k " is a proportionality constant that gives S appropriate units for our calculations.) Notice that the more microstates there are, the greater the entropy is. Therefore, a macrostate with a high probability (e.g. a mixed state) has a large entropy. We now modify our previous deduction to say that a spontaneous process produces the final state of greatest entropy. (Following modifications added below, this statement forms the Second Law of Thermodynamics.)

It would seem that we could use W for our calculations and that the definition of the new function S is unnecessary. However, the following reasoning shows that W is not a convenient function for calculations. We consider two identical glasses of water at the same temperature. We expect that the value of any physical property for the water in two glasses is twice

the value of that property for a single glass. For example, if the enthalpy of the water in each glass is H_1 , then it follows that the total enthalpy of the water in the two glasses together is $H_{\text{total}} = 2H_1$. Thus, the enthalpy of a system is proportional to the quantity of material in the system: if we double the amount of water, we double the enthalpy. In direct contrast, we consider the calculation involving W for these two glasses of water. The number of microstates of the macroscopic state of one glass of water is W_1 , and likewise the number of microstates in the second glass of water is W_1 . However, if we combine the two glasses of water, the number of microstates of the total system is found from the product $W_{\text{total}} = W_1 \times W_1$, which does not equal $2W_1$. In other words, W is not proportional to the quantity of material in the system. This is inconvenient, since the value of W thus depends on whether the two systems are combined or not. (If it is not clear that we should multiply the W values, consider the simple example of rolling dice. The number of states for a single die is 6, but for two dice the number is $6 \times 6 = 36$, not $6 + 6 = 12$.)

We therefore need a new function $S(W)$, so that, when we combine the two glasses of water, $S_{\text{total}} = S_1 + S_1$. Since $S_{\text{total}} = S(W_{\text{total}})$, $S_1 = S(W_1)$, and $W_{\text{total}} = W_1 \times W_1$, then our new function S must satisfy the equation

$$S(W_1 \times W_1) = S(W_1) + S(W_1)$$

The only function S which will satisfy this equation is the logarithm function, which has the property that $\ln(x \times y) = \ln(x) + \ln(y)$. We conclude that an appropriate state function that measures the number of microstates in a particular macrostate is

$$S = k \ln W$$

Observation 2: Absolute Entropies

It is possible, though exceedingly difficult, to calculate the entropy of any system under any conditions of interest from the equation $S = k \ln W$. It is also possible, using more advanced theoretical thermodynamics, to experimentally determine S by measuring heat capacities and enthalpies of phase transitions. Values of S determined experimentally, often referred to

as "absolute" entropies, have been tabulated for many materials at many temperatures. A few examples are given in Table 1 measured at pressure of 1 atm. (The superscript ° on S indicates standard pressure. It turns out that, for gases, the entropy depends significantly on the pressure.) Our goal is to analyze these data in the context of Equation (1).

There are several interesting trends observed in Table 1. First, if we compare the entropy of the gaseous form of a substance to either its liquid or solid form at the same temperature, we find that the gas always has a substantially greater entropy. This makes sense from Equation (1): the molecules in the gas phase occupy a very much larger volume. There are many more possible locations for each gas molecule and thus many more arrangements of the molecules in the gas. This means that W should be larger for a gas, and therefore the entropy of a gas is greater than that of the corresponding liquid or solid.

Second, we can see in the table that the entropy of a liquid is always greater than that of the corresponding solid. This is understandable from our kinetic molecular view of liquids and solids. Although the molecules in the liquid occupy a comparable volume to that of the molecules in the solid, each molecule in the liquid is free to move throughout this entire volume. The molecules in the solid are relatively fixed in location. Therefore, the number of arrangements of molecules in the liquid is significantly greater than that in the solid, so the liquid has greater entropy by Equation (1).

	T (°C)	S°(J/mol·°C)
H ₂ O (g)	25	188.8
H ₂ O (l)	25	69.9
H ₂ O (l)	0	63.3

	T (°C)	S°(J/mol·°C)
H ₂ O (s)	0	41.3
NH ₃ (g)	25	192.4
HN ₃ (l)	25	140.6
HN ₃ (g)	25	239.0
O ₂ (g)	25	205.1
O ₂ (g)	50	207.4
O ₂ (g)	100	211.7
CO (g)	25	197.7
CO (g)	50	200.0
CO ₂ (g)	24	213.7
CO ₂ (g)	50	216.9
Br ₂ (l)	25	152.2
Br ₂ (g)	25	245.5
I ₂ (s)	25	116.1
I ₂ (g)	25	260.7
CaF ₂ (s)	25	68.9
CaCl ₂ (s)	25	104.6

	T (°C)	S°(J/mol·°C)
CaBr ₂ (s)	25	130
C ₈ H ₁₈ (l)	25	361.1

Absolute Entropies of Specific Substances

Third, the data show that the entropy of a substance increases with increasing temperature. We have previously found that the temperature of a substance is a measure of the average kinetic energy of the molecules in the substance. In a solid or liquid, then, increasing the temperature increases the total kinetic energy available to the molecules. The greater the energy, the more ways there are to distribute this energy amongst the molecules. Although we have previously only referred to the range of positions for a molecule as affecting W , the range of energies available for each molecule similarly affects W . As a result, as we increase the total energy of a substance, we increase W and thus the entropy.

Fourth, the entropy of a substance whose molecules contain many atoms is greater than that of a substance composed of smaller molecules. This is somewhat new to us. We have discussed the structures of molecules in terms of specific geometries. However, these structures are not rigid. The atoms within a molecule vibrate, or wiggle, back and forth about the geometry the molecule. The more atoms there are in a molecule, the more ways there are for those atoms to wiggle with respect to each other. With this greater internal flexibility, W is larger when there are more atoms, so the entropy is greater.

Fifth, the entropy of a substance with a high molecular weight is greater than that of substance with a low molecular weight, even if the number of atoms is the same or nearly the same. This result is a harder to understand because it does not relate to the positions that the atoms can occupy. It is clear that the number of arrangements of the molecules is not affected by the masses of the molecules. However, one way to describe the state of a molecule would be to specify its position and its momentum. (In quantum mechanics, we know that it is not possible to specify both the position and

the momentum, but this non-quantum explanation is easier to visualize than the quantum explanation.) The range of momenta available for a heavier molecule is greater than for a lighter one, even at the same temperature. To see why, recall that the momentum of a molecule is $p = mv$ and the kinetic energy is $KE = (1/2)mv^2 = (1/2m)p^2$. Therefore, the maximum momentum available at a fixed temperature and a fixed total kinetic energy KE is $p = \sqrt{2mKE}$. When m is larger for larger mass molecules, the range of momenta is greater for heavier particles. With more possible states for each molecule, W and the entropy are both larger.

Observation 3: Condensation and Freezing

We have concluded from our observations of spontaneous mixing that a spontaneous process always produces the final state of greatest probability and greatest entropy. A few simple observations reveal that this is not entirely correct and that our conclusion needs some careful refinement. For example, we have observed that the entropy of liquid water is greater than that of solid water. This makes sense in the context of Equation (1), since the kinetic theory indicates that liquid water has a greater value of W . Nevertheless, we observe that liquid water spontaneously freezes at temperatures below 0 °C. This process clearly displays a decrease in entropy and therefore evidently a shift from a more probable state to a less probable state. This appears to directly contradict our conclusion.

Similarly, we expect to find condensation of water droplets from steam when steam is cooled. On days of high humidity, water spontaneously liquefies from the air on cold surfaces such as the outside of a glass of ice water or the window of an air conditioned building. In these cases, the transition from gas to liquid is clearly from a higher entropy phase to a lower entropy phase, which does not seem to follow our reasoning thus far. In fact, our reasoning would imply that ice should always melt and water should always evaporate, no matter what the conditions are. We have either left something out of our reasoning, or we have made a serious mistake. Before abandoning our reasoning, let's recall that our previous conclusions concerning entropy and probability increases were quite compelling. We should be reluctant to abandon them. What did we overlook?

One thing we have failed to take into consideration is that these phase transitions involve changes of energy and thus heat flow. Condensation of gas to liquid and freezing of liquid to solid both involve evolution of heat. This heat flow is of consequence because our observations also revealed that the entropy of a substance can be significantly increased by elevating its temperature.

One way to preserve our conclusions about spontaneity and entropy is to place a condition on their validity: a spontaneous process produces the final state of greatest probability and entropy provided that the process does not involve the evolution of heat. This is an unsatisfying result, however, since most physical and chemical processes involve heat transfer. As an alternative, we can force the process not to evolve heat by isolating the system undergoing the process: no heat can be released if there is no sink to receive the heat, and no heat can be absorbed if there is no source of heat. Therefore, we conclude from our observations that, for a spontaneous process in an isolated system the entropy always increases and leads us to the final state of greatest probability and entropy. This is one statement of the Second Law of Thermodynamics:

$\Delta S > 0$ *spontaneous process in an isolated system*

It is interesting to consider one particular “isolated system,” which is the entire universe. Since no energy or matter can transfer in or out of the universe, the universe qualifies as “isolated.” So, another statement of the Second Law of Thermodynamics is:

$\Delta S_{\text{universe}} > 0$ *for any spontaneous process*

Though interesting and quite general, this statement is not yet all that useful because calculating S for the entire universe seems very difficult. In the next Concept Development Study, we will develop a means to do that calculation fairly easily.

Observation 4: Heat Transfer and Entropy Changes

We will begin with a simple and common observation about heat flow. Let's take two pieces of metal of the same mass. It doesn't matter what type of metal or what mass, so let's say 100.0 g of copper. Let's heat one of the samples (call it sample A) to 100 °C and cool the other (call it sample B) to 0 °C. Then let's place them in contact with each other but insulated from everything surrounded them. We know from everyday experience what is going to happen, but of course, when we run the experiment, the cold metal B warms up, the hot metal A cools off, and both pieces of metal stop changing temperature only when they come to the same temperature, in this case, 50 °C. We say that they have reached "thermal equilibrium."

The approach to thermal equilibrium is clearly a spontaneous process: it happens automatically, and indeed there is nothing we can do to stop it other than to isolate the two pieces of metal from each other. Since this is a spontaneous process and since we isolated the two pieces of metal from their surroundings, then the work of the previous study tells us that, in total for system consisting of the two pieces of metal, $\Delta S > 0$.

All that has happened is the transfer of heat from one piece of metal to the other. No chemical reactions or phase changes have occurred and there has been no rearrangement of the atoms in the metal samples. Why did this heat transfer increase the entropy? We know from our previous study that raising the temperature of a sample by adding heat increases the entropy of the sample. Let's say that the amount of heat transferred into sample B was q . The energy of sample B goes up by q during the heat transfer. And therefore the entropy of B must go up.

However, by conservation of energy, this same amount of heat q must also transfer out of sample A. The energy of sample A goes down by q during the heat transfer. And therefore the entropy of A must go down. Since the heat transfer is the same and the types and masses of the metal samples are the same, it would seem that the entropy increase of B should be exactly equal to the entropy decrease of A, in which case the total entropy change should be zero. But we know that this is not true, because the transfer of heat is a spontaneous process in an isolated system, so $\Delta S > 0$.

This can only mean that the entropy increase of the cold sample B must be larger than the entropy decrease of the hot sample A as they approach

thermal equilibrium. This tells us that the quantity of heat alone is not enough to predict the entropy change associated with heat transfer. We must also know the temperature to predict the entropy change.

Our observations also tell us that the entropy change is greater for the lower temperature sample. Entropy change and temperature are therefore inversely related to each other. Adding heat to a cold sample produces a greater entropy change than adding heat to a hot sample. We can conclude all of this based just upon observing that heat spontaneously flows from a hot piece of metal to a cold piece of metal. What is harder to conclude is what the exact inverse relationship is. With much more effort and mathematical reasoning, we can show that the correct inverse relationship between entropy change and temperature is the simplest inverse relationship, namely an inverse proportion:

$$\Delta S = q/T \text{ for transfer of heat } q \text{ at temperature } T$$

This equation works when the temperature is held constant during the heating process. If the temperature is not held constant, we have to do an integral of $1/T$ from the initial temperature to the final temperature to calculate ΔS . That is not important for our purposes here. But it is interesting to ask how we can heat a body without changing its temperature. We will discuss this in the next section.

Observation 5: Heat Transfer during Chemical or Physical Processes

The results of the previous observations and reasoning are important in all cases where heat is transferred, not just in heat transfers involving substances at two different temperatures. Let's think back to our goal here. How can the Second Law be applied to a process in a system that is not isolated? We would like to understand how it is possible for a process in a non-isolated system to be spontaneous when $\Delta S < 0$ for the system in that process. A good example is the freezing of water at temperatures below 0 °C. What is so special about 0 °C? Why is it that below this temperature, the freezing process becomes spontaneous even though $\Delta S < 0$?

Let's observe the entropy changes for freezing water at $-10\text{ }^{\circ}\text{C}$, which we know to be a spontaneous process. First, let's calculate the ΔS for the process $\text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O}(s)$ near $0\text{ }^{\circ}\text{C}$. We can do this from a table of absolute entropies, such as in the previous Concept Development Study. At $0\text{ }^{\circ}\text{C}$, S for $\text{H}_2\text{O}(l) = 63.3\text{ J/mol}\cdot\text{K}$ and S for $\text{H}_2\text{O}(s) = 41.3\text{ J/mol}\cdot\text{K}$, so for the freezing of water, $\Delta S = -22.0\text{ J/mol}\cdot\text{K}$. As expected, this is less than zero.

We know from our previous observation that, since freezing releases heat into the surroundings, then freezing must increase the entropy of the surroundings. Let's calculate this change in entropy, $\Delta S_{\text{surroundings}}$. We will assume quite reasonably and fairly generally that the only effect on the entropy of the surroundings of the freezing taking place in the system is the transfer of heat from the system to the surroundings. There is no other exchange or interaction which happens. We might expect that releasing heat into the surroundings would change the temperature of the surroundings. However, the surroundings are typically huge (e.g. the entire room in which the process occurs) that the effect of the heat transfer into the surroundings does not make a measurable change in the surrounding temperature. The same is true when energy is absorbed from the surroundings into the system.

From our Concept Development Study on energy changes, we can calculate the heat transfer for a process occurring under constant pressure from the enthalpy change for the process, $q = \Delta H^{\circ}$. By conservation of energy, the heat flow out of or into the surroundings must be $-\Delta H^{\circ}$. From our previous observation, the entropy change resulting from this transfer of heat is

$$\Delta S^{\circ}_{\text{surroundings}} = q/T = -\Delta H^{\circ}/T$$

In this equation, ΔH is the enthalpy change for the system, which is why there is a negative sign in this equation. Notice that, if the process releases energy as is the case in freezing, $\Delta H^{\circ} < 0$ so $\Delta S^{\circ}_{\text{surroundings}} > 0$.

For $\text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O}(s)$, $\Delta H^{\circ} = \Delta H^{\circ}_{\text{f}}(\text{H}_2\text{O}(s)) - \Delta H^{\circ}_{\text{f}}(\text{H}_2\text{O}(l))$. From the data tables, we can calculate that $\Delta H^{\circ} = -6.02\text{ kJ/mol}$. As expected, this is less than zero. From this, we can calculate that at $-10\text{ }^{\circ}\text{C} = 263\text{ K}$, $\Delta S^{\circ}_{\text{surroundings}} = 22.9\text{ J/mol}\cdot\text{K}$. Again, as expected, this is greater than zero.

We now come to the most important observation: the entropy increase of the surroundings is greater than the entropy decrease of the water that is freezing. This means that, in total, the entropy change for both system and surroundings is positive.

The conclusion of this observation is that, in analyzing whether a process is spontaneous or not, we must consider both the change in entropy of the system undergoing the process and the effect of the heat released or absorbed during the process on the entropy of the surroundings. In other words, we have to consider the entropy change of the universe:

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$

We can say then that

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = \Delta S_{\text{system}} - \Delta H_{\text{system}}/T$$

The last part of this equation says that we can calculate the entropy change of the universe from calculations that involve only entropy and energy changes in the system. This sounds very doable! For every spontaneous process, $\Delta S_{\text{universe}} > 0$, so for every spontaneous process:

$$\Delta S_{\text{system}} - \Delta H_{\text{system}}/T > 0$$

In this inequality, the entropy change and the enthalpy change are both for the system, so the subscripts are now not needed and we can drop them to make the equation easier to read.

$$\Delta S - \Delta H/T > 0 \text{ any spontaneous process}$$

The fact that the temperature appears in this equation is very interesting. Remember why it is there in the denominator: the effect on the entropy of the heat exchange with the surroundings is smaller when the temperature is larger.

This also suggests that we try our calculation with a different temperature. What if the temperature is 10 °C, above the freezing point? In this case, we observe experimentally that the melting of solid ice is spontaneous. Let's do

the calculation of the inequality above for the process $\text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O}(s)$ at 10°C . As before, $\Delta H^\circ = -6.02 \text{ kJ/mol}$ and $\Delta S^\circ = -22.0 \text{ J/mol}\cdot\text{K}$, but now $T = 283\text{K}$. We get that

$$\Delta S^\circ - \Delta H^\circ/T = -0.73 \text{ J/mol}\cdot\text{K} < 0$$

We find a negative number, telling us that freezing water is not spontaneous at 10°C . More importantly, we know that the reverse process of melting ice is spontaneous at 10°C . This means that, if $\Delta S - \Delta H/T < 0$, the reverse process is spontaneous.

Now we know what is so special about the temperature 0°C . Below that temperature, $\Delta S^\circ - \Delta H^\circ/T > 0$ for the freezing of water, and above that temperature $\Delta S^\circ - \Delta H^\circ/T < 0$ for the freezing of water, so $\Delta S^\circ - \Delta H^\circ/T > 0$ for the melting of ice.

What happens at 0°C ? It is easy to calculate that $\Delta S^\circ - \Delta H^\circ/T = 0$ at that temperature. Of course, at that temperature at standard pressure, water and ice are in equilibrium. This is a very important observation: when $\Delta S - \Delta H/T = 0$, the process is at equilibrium. We will develop this observation in much greater detail in the next Concept Development Study.

Review and Discussion Questions

1. Each possible sequence of the 52 cards in a deck is equally probable. However, when you shuffle a deck and then examine the sequence, the deck is never ordered. Explain why in terms of microstates, macrostates, and entropy.
2. Assess the validity of the statement, "In all spontaneous processes, the system moves toward a state of lowest energy." Correct any errors you identify.
3. Recalling the discussion of the freezing point of water, determine what must be true about ΔH° and ΔS° for a solid to have a freezing point much higher than that of water. Similarly, determine what must be true about ΔH° and ΔS° for a solid to have a freezing point much lower than that of water.

4. Predict the sign of the entropy for the reaction $2 \text{H}_2 (\text{g}) + \text{O}_2 (\text{g}) \rightarrow 2 \text{H}_2\text{O} (\text{g})$. Give an explanation, based on entropy and the Second Law, of why this reaction occurs spontaneously.
5. For the reaction $\text{H}_2(\text{g}) \rightarrow 2 \text{H}(\text{g})$, predict the sign of both ΔH° and ΔS° . Based on your knowledge of hydrogen, which of these two terms is probably dominant in determining whether the reaction is spontaneous. What would you predict would be the effect of lowering the temperature? Explain.

Free Energy and Thermodynamic Equilibrium

Introduction

In the previous study, we observed and applied the Second Law of Thermodynamics to predict when a process will be spontaneous. For example, the melting of solid water at a temperature above 0 °C at 1 atm pressure is a spontaneous process, and thermodynamics predicts this very accurately. However, over the course of several Concept Development Studies, we focused on processes at equilibrium, rather than processes occurring spontaneously. These include phase equilibrium, solubility equilibrium, reaction equilibrium, and acid-base equilibrium. Interestingly, we can use our understanding of spontaneous processes to make predictions about equilibrium processes too.

To begin, we need to be clear about what we mean by a “spontaneous process” versus an “equilibrium process.” At equilibrium, the macroscopic properties we observe (temperature, pressure, partial pressures, concentrations, volume) do not change. We have developed a model to describe equilibrium based on the idea of dynamic equilibrium, meaning that at equilibrium, there are forward and reverse reactions occurring at the molecular level at the same rate. However, this is not what we mean by “spontaneous process,” since the forward and reverse reactions exactly offset one another in a dynamic equilibrium. By contrast, in a spontaneous process, we observe macroscopic changes: partial pressures of reactants or products are increasing, concentrations are increasing or decreasing, the temperature or volume is changing, etc. This means that the forward and reverse reactions at the molecular level do not offset one another, and real macroscopic changes occur.

As we have discovered, during a spontaneous process the entropy of the universe increases. When a process comes to equilibrium, there are no spontaneous processes, so a reaction at equilibrium does not increase the entropy of the universe. We can combine these two ideas to say that, as a process spontaneously approaches equilibrium, the entropy of the universe continually increases until equilibrium is reached, at which point the process no longer increases the entropy of the universe. This gives us a way

to predict the conditions under which a process will reach equilibrium. We will develop this approach in this Concept Development Study.

We will have to be careful in applying the Second Law of Thermodynamics in calculations. So far, we have only observed and tabulated values of the “absolute entropy,” S° , at standard pressures and concentrations. We can use these to make predictions about processes at standard pressure and concentrations. But we know that phase transitions and reactions almost always come to equilibrium at partial pressures not equal to 1 atm and concentrations not equal to 1 M. Therefore, we must be careful when we interpret calculations of ΔS using S° values. And to understand the conditions at equilibrium, we must determine how to calculate S values for non-standard conditions. Only then will we be able to apply the Second Law of Thermodynamics at equilibrium conditions.

Foundation

We have come a long way to reach this point in our studies, so we have a substantial foundation to build on. We know all the elements of the Atomic Molecular Theory, including the models for molecular structure and bonding, and we have developed the postulates of the Kinetic Molecular Theory. We have observed and defined phase transitions and phase equilibrium, and we have also observed equilibrium in a variety of reaction systems, including acids and bases. We will assume an understanding of the energetics of chemical reactions, including the idea of a “state function” and the concept of Hess’ Law.

In the previous study, we developed the expression $\Delta S - \Delta H/T > 0$ as a predictor of whether a process will be spontaneous. Chemists generally rewrite this inequality in a different and somewhat more convenient form by multiplying both sides by $-T$:

$$-T\Delta S + \Delta H < 0$$

This is the same inequality, but take notice of the “less than” sign which replaced the “greater than” sign as a result of multiplying by $-T$.

Both terms in this inequality have units of energy, so $\Delta H - T\Delta S$ is often referred to as an energy. However, it is important to remember that this combination of terms arises from calculating the changes in entropy of the system and its surroundings, and the “less than” sign arises from the Second Law of Thermodynamics which deals with entropy and not energy. As such, chemists refer to this combination of terms as the “free energy” rather than the energy. Specifically, we define a new term as $G = H - TS$, which is also called the “Gibbs free energy.” If the temperature of a process is constant, then for that process $\Delta G = \Delta H - T\Delta S$. This means that

$\Delta G < 0$ for any spontaneous process at constant T and P.

This might look and sound new and complicated, but this is just the Second Law of Thermodynamics in a succinct and convenient form. To see this, let’s recall that

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = \Delta S - \Delta H/T$$

If we multiply this equation by $-T$, we get

$$-T\Delta S_{\text{universe}} = -T\Delta S + \Delta H = \Delta G$$

These equations show that the change in the free energy is just the change in the entropy of the universe multiplied by $-T$. Since $\Delta S_{\text{universe}} > 0$, then $\Delta G < 0$. As such, when you see G for “free energy,” you might find it convenient to think of it as the “negative entropy of the universe.” For that reason, during a spontaneous process, the free energy of the system always decreases. We will use this notation alternately with the entropy notation.

Observation 1: Thermodynamic Description of Phase Equilibrium

In the previous study, we carefully analyzed the freezing of water as an interesting example of a spontaneous process for which $\Delta S^\circ < 0$ but for which $\Delta S^\circ - \Delta H^\circ/T > 0$. The discussion above tells us that, when the freezing of water is at equilibrium, then $\Delta S^\circ - \Delta H^\circ/T = 0$. We should be able to solve this equation for T to predict the temperature at 1 atm when liquid

water and solid water are in equilibrium. We can calculate $\Delta S^\circ = S^\circ_{\text{liquid}} - S^\circ_{\text{solid}} = 22.0 \text{ J/mol}\cdot\text{K}$, and $\Delta H^\circ = \Delta H^\circ_f(\text{liquid}) - \Delta H^\circ_f(\text{solid}) = 6.01 \text{ kJ/mol}$. When we solve for T we get $T = 273 \text{ K}$, which is of course the melting point temperature of water. This calculation shows the power of our predictions from the Second Law of Thermodynamics. Not only can we determine what processes are spontaneous, but we also determine the conditions necessary for a process to come to equilibrium!

We next want to consider phase equilibrium between liquid and vapor. Our goal is to predict the temperatures and pressures at which equilibrium exists between liquid water and water vapor. Let's start with the temperature at which liquid water and water vapor are at equilibrium when the pressure is 1 atm. We know the observed answer to this; it is the boiling point of water, 100 °C.

Based on our reasoning, $\Delta S^\circ - \Delta H^\circ/T = 0$ at the boiling point temperature at 1 atm pressure. Plugging in $\Delta S^\circ = 118.9 \text{ J/K}\cdot\text{mol}$ and $\Delta H^\circ = 44.0 \text{ kJ/mol}$, we can solve for T to find the equilibrium temperature at 370 K, which is very close to the observed boiling point of 373 K. (The slight error is that the values of ΔS° and ΔH° depend somewhat on the temperature, and we used values from data collected at 25 °C. If we use the accurate values, we can predict the boiling point of water exactly.)

At other temperatures and pressures, the study of phase equilibrium involving vapor becomes more complicated because the entropy of a gas depends strongly on the pressure of the gas. This means that we cannot simply use the values of S° , which are valid at 1 atm pressure. We'll illustrate this by analyzing the thermodynamics of the evaporation of water. At equilibrium, this should lead us to predict the vapor pressure of water and, relatedly, the boiling point of water, but we have some work to do first.

As we recall, the entropy of one mole of vapor is much greater than the entropy of the same amount of liquid. A look back at Table 1 shows that, at 25 °C, the entropy of one mole of liquid water is 69.9 J/K, whereas the entropy of one mole of water vapor at 1 atm is 188.8 J/K. This means that for the evaporation of one mole of liquid water at room temperature and 1 atm pressure, $\Delta S^\circ > 0$. We might think that this means that a mole of liquid water at 25 °C should spontaneously convert into a mole of water vapor,

since this process would greatly increase the entropy of the water. We know, of course, that this does not happen. Learning from our previous study, we must also consider the energy associated with evaporation. The conversion of one mole of liquid water into one mole of water vapor results in the absorption of 44.0 kJ of energy from the surroundings. Recall that this loss of energy from the surroundings results in a significant decrease in the entropy of the surroundings. We combine both of these factors by calculating $\Delta S - \Delta H/T$ for the evaporation of liquid water at 25 °C:

$$\Delta S^\circ - \Delta H^\circ/T = 118.9 \text{ J/K}\cdot\text{mol} - (44.0 \text{ kJ/mol})/(298 \text{ K}) = - 28.9 \text{ J/K}\cdot\text{mol}$$

We can repeat this calculation in terms of the free energy change:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\Delta G^\circ = 44,000 \text{ J/mol} - (298.15\text{K})(118.9\text{J/K mol})$$

$$\Delta G^\circ = 8.55 \text{ kJ/mol} > 0$$

How do we interpret these numbers? Since $\Delta S^\circ - \Delta H^\circ/T < 0$ and $\Delta G^\circ > 0$, these calculations tell us that the evaporation of water at 25 °C is not spontaneous. But note carefully that these calculations use the values of entropy and enthalpy changes valid for 1 atm pressure of the water vapor. So, a careful interpretation of these inequalities tells us that evaporation of water at 25 °C is not spontaneous when the pressure of the water vapor is 1 atm. We can also conclude from this result that the reverse process is spontaneous: the condensation of water vapor to liquid is spontaneous at 25 °C when the pressure of the water vapor is 1 atm. These predictions are all correct and match experimental observations. Although liquid water does have a vapor pressure at 25 °C, it is at 23.8 torr, very far below 1.00 atm. So water vapor at 1 atm pressure will condense spontaneously down to a low but non-zero pressure.

Now let's determine the pressure at 25 °C at which the liquid and vapor are in equilibrium. If we cool the liquid-vapor equilibrium from 100 °C to 25 °C while maintaining equilibrium, we observe that the vapor pressure of the water drops to 23.8 torr. This means that, when the temperature is 25 °C and the pressure is 23.8 torr, $\Delta G = 0$ and $\Delta S - \Delta H/T=0$. We have already

calculated that 8.55 kJ/mol, and therefore is not zero, so apparently ΔG depends on the pressure. Since $\Delta G = \Delta H - T\Delta S$, then either ΔS or ΔH changes when we change the pressure. Experiments tell us that pressure has little effect on ΔH . This makes sense: in the gas phase, the molecules do not interact, so unless we increase the pressure enormously, changing the separation of the gas particles does not affect their energy. ΔS , it turns out, does depend strongly on pressure.

Why does entropy depend so strongly on pressure? From Boyle's Law, we know that 1 mole of water vapor occupies a much larger volume at a low pressure like 23.8 torr than it does at the considerably higher vapor pressure of 1 atm. In that much larger volume, the water molecules have a much larger space to move in, so the number of microstates for the water molecules must be larger in a larger volume. Therefore, the entropy of one mole of water vapor is larger when the volume is larger and the pressure is lower. This means that ΔS for the evaporation of one mole of water is greater when that one mole evaporates to a lower pressure.

We need to calculate how much the entropy of one mole of a gas increases as we decrease the pressure. To do so, we will use our equation $S = k \ln W$. We can reasonably assume that the number of microstates W for the gas molecules is proportional to the volume V , because the larger the volume, the more places there are for the molecules to be. From the previous study, the entropy is given by $S = k \ln W$, which means that S must also be proportional to $\ln V$. Therefore, we can say that

$$S(V_2) - S(V_1) = R \ln W_2 - R \ln W_1 = R \ln W_2 / W_1 = R \ln V_2 / V_1$$

Since we are interested in the variation of S with pressure rather than volume, we can use Boyle's Law, which states that for a fixed temperature, the volume of one mole of gas is inversely proportional to its pressure. This tells us how entropy varies with pressure:

$$S(P_2) - S(P_1) = R \ln P_1 / P_2 = - R \ln P_2 / P_1$$

Let's apply this to water vapor. We know that the entropy of one mole of water vapor at 1.00 atm pressure is $S^\circ = 188.8 \text{ J/K}$. For a pressure of 23.8

torr = 0.0313 atm, Equation (5) shows that $S(23.8 \text{ torr}) = 217.6 \text{ J/K}$ for one mole of water vapor. S changes quite a lot as P changes!

From this, we can calculate ΔS for the evaporation of one mole of water vapor to 23.8 torr at 25 °C: $\Delta S = S(\text{water vapor at 23.8 torr}) - S(\text{liquid water}) = 217.6 \text{ J/mol}\cdot\text{K} - 69.9 \text{ J/mol}\cdot\text{K} = 147.6 \text{ J/mol}\cdot\text{K}$.

At equilibrium, $\Delta S - \Delta H/T = 0$. When we plug in this value of ΔS and the previous value of ΔH as well as the temperature 298.15 K, we get 0.00 J/mol·K. Or we can calculate $\Delta G = \Delta H - T\Delta S = 44.0 \text{ kJ} - (298.15\text{K})(147.6 \text{ J/K}) = 0.00 \text{ kJ}$. Either of these is the condition we expected for equilibrium. This confirms our observations.

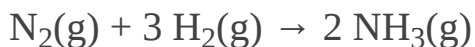
We can conclude that the evaporation of water when no vapor is present initially is a spontaneous process with $\Delta G < 0$, and the evaporation continues until the water vapor has reached the equilibrium vapor pressure, at which point $\Delta G = 0$. Equivalently, the condensation of water vapor when the pressure is 1 atm is spontaneous with $\Delta G < 0$ until enough water vapor has condensed to reach the equilibrium vapor pressure, at which point again $\Delta G = 0$. Thermodynamics tells us exactly what the conditions are for phase equilibrium!

Observation 2: Thermodynamic description of reaction equilibrium

Now that we have developed a thermodynamic understanding of phase equilibrium, it is even more useful to examine the thermodynamic description of reaction equilibrium. We want to understand why the reactants and products come to equilibrium at the specific concentrations and pressures that are observed.

Recall that $\Delta G = \Delta H - T\Delta S < 0$ for a spontaneous process, and $\Delta G = \Delta H - T\Delta S = 0$ at equilibrium. From these relations, we would predict that most (but not all) exothermic processes with $\Delta H < 0$ are spontaneous, because all such processes increase the entropy of the surroundings when they occur. Similarly, we would predict that most (but not all) processes with $\Delta S > 0$ are spontaneous.

We try applying these conclusions to synthesis of ammonia



at 298 K, for which we find that $\Delta S^\circ = 198 \text{ J/mol}\cdot\text{K}$. Note that $\Delta S^\circ < 0$ because the reaction reduces the total number of gas molecules during the ammonia synthesis, thus reducing W , the number of ways of arranging the atoms in these molecules. $\Delta S^\circ < 0$ suggests that N_2 and H_2 should not react at all to produce NH_3 . On the other hand, $\Delta H^\circ = -92.2 \text{ kJ/mol}$ from which we can calculate that $\Delta G^\circ = -33.0 \text{ kJ/mol}$ at 298 K. This suggests that N_2 and H_2 should react completely to form NH_3 . But in reality, we learned in the Concept Development Study of reaction equilibrium that this reaction comes to equilibrium, with N_2 , H_2 , and NH_3 all present. We determined the equilibrium constant

$$K_p = \frac{P(\text{NH}_3)^2}{P(\text{N}_2) \cdot P(\text{H}_2)^3} = 6 \times 10^5$$

Why does the reaction come to equilibrium without fully consuming all of the reactants?

The answer, just as before, lies in a more careful interpretation and application of the values given: ΔS° , ΔH° , and ΔG° are the values for this reaction at standard conditions, which means that all of the gases in the reactants and products are taken to be at 1 atm pressure. Thus, the fact that $\Delta G^\circ < 0$ for Reaction (6) at standard conditions means that, if all three gases are present at 1 atm pressure, the reaction will spontaneously proceed to increase the amount of NH_3 .

From this analysis, we can say that, since $\Delta G^\circ < 0$ for Reaction (6), reaction equilibrium results in the production of more product and less reactant than at standard pressures. This is consistent with our previous measurement that $K_p = 6 \times 10^5$, a number much, much larger than 1. As a result, we can say that Reaction (6) is “thermodynamically favorable,” meaning that thermodynamics accurately predicts that the equilibrium favors products over reactants.

Thermodynamics can even provide a quantitative prediction of the equilibrium constant. Recall that the condition for equilibrium is that $\Delta G = 0$ and that ΔG depends on the pressures of the gases in the reaction mixture, because ΔS depends on these pressures. Above, we showed that the entropy of a gas changes with the pressure by

$$S(P) - S^\circ = -R \ln(P/(1 \text{ atm}))$$

For the reaction of N_2 and H_2 to form NH_3 , let's use the above equation to calculate ΔS for whatever partial pressures at which the reactants and products happen to be.

$$\Delta S = 2S_{NH_3} - 3S_{H_2} - S_{N_2}$$

$$\Delta S = \Delta S^\circ - 2R \ln(P_{NH_3}) + 3R \ln(P_{H_2}) + R \ln(P_{N_2})$$

$$\Delta S = \Delta S^\circ - R \ln(P_{NH_3}^2/P_{H_2}^3 P_{N_2})$$

In the last step, we used the properties of logarithms to combine all the terms and to use the coefficients as exponents. The term in parentheses looks just like the equilibrium constant expression. However, it is not equal to the equilibrium constant because these partial pressures are not necessarily at equilibrium – they are whatever we choose them to be. As such, we call this term in parentheses the “reaction quotient,” designated Q :

$$Q = (P_{NH_3}^2/P_{H_2}^3 P_{N_2})$$

So,

$$\Delta S = \Delta S^\circ - R \ln Q$$

It turns out that this is a general expression for any reaction involving gases, provided that we form Q from the balanced equation with appropriate exponents. It also turns out that this expression works for any reaction involving solutes or ions in solution provided that we take the concentrations of the solutes or ions in solution with the appropriate exponents.

We can use this expression to calculate ΔG , if we recall that ΔH does not depend on pressure:

$$\Delta G = \Delta H - T\Delta S = \Delta H^\circ - T(\Delta S^\circ - R\ln Q)$$

$$\Delta G = \Delta H^\circ - T\Delta S^\circ + RT\ln Q$$

Or, finally,

$$\Delta G = \Delta G^\circ + RT\ln Q$$

This last equation is an exceptionally powerful relationship for predicting in what direction a reaction will proceed spontaneously and when the reaction will come to equilibrium.

Let's first consider the reaction at equilibrium. At equilibrium, $\Delta G = 0$. Also $Q = K_p$ by definition of Q and K_p . So

$$\Delta G^\circ = -RT\ln K_p$$

This is a remarkable equation as it relates a thermodynamic quantity involving enthalpy changes and entropy changes to the experimentally observed reaction equilibrium constant. In fact, this proves why the equilibrium constant we experimentally observed is indeed a constant. Because this result turns out to be general, we can drop the subscript "p" referring to partial pressures. K is then any equilibrium constant.

If ΔG° is a large negative number, K will be a large positive number and the reaction is thermodynamically favorable. If ΔG° is a large positive number, K will be a number much less than one, and the reaction is thermodynamically unfavorable.

Let's plug the last equation for ΔG° into the immediately preceding equation for ΔG :

$$\Delta G = -RT\ln K + RT\ln Q = RT\ln(Q/K)$$

We can use this equation to predict when a reaction will be spontaneous from reactants to products, when it will be spontaneous from products to

reactants, and when it will be at equilibrium. ΔG will be negative when $Q < K$, or in other words, when the numerator in Q is too small and the denominator is too large to equal K . This means we need more products and less reactants, so the reaction proceeds spontaneously forward, as we expect when ΔG is negative. Similarly, ΔG will be positive when $Q > K$, and the reaction proceeds spontaneously in reverse. Only when $Q = K$ will we have $\Delta G = 0$, so equilibrium requires that $Q = K$. This is what we observed experimentally. Therefore, thermodynamics both predicts and explains the position of equilibrium for chemical reactions. This is an amazing result!

Note that the thermodynamic description of equilibrium and the dynamic description of equilibrium are complementary. Both predict the same equilibrium. In general, the thermodynamic arguments give us an understanding of the conditions under which equilibrium occurs, and the dynamic arguments help us understand how the equilibrium conditions are achieved.

Review and Discussion Questions

1. Why does the entropy of a gas increase as the volume of the gas increases? Why does the entropy decrease as the pressure increases?
2. For each of the following reactions, calculate the values of ΔS° , ΔH° , and ΔG° at $T = 298\text{ K}$ and use these to predict whether equilibrium will favor products or reactants at $T = 298\text{ K}$. Also calculate K_p .
 - a. $2\text{CO(g)} + \text{O}_2\text{(g)} \rightarrow 2\text{CO}_2\text{(g)}$
 - b. $\text{O}_3\text{(g)} + \text{NO(g)} \rightarrow \text{NO}_2\text{(g)} + \text{O}_2\text{(g)}$
 - c. $2\text{O}_3\text{(g)} \rightarrow 3\text{O}_2\text{(g)}$
3. For each of the reactions in Question 3, predict whether increases in temperature will shift the reaction equilibrium more towards products or more towards reactants.
4. Show that for a given set of initial partial pressures where Q is larger than K_p , the reaction will spontaneously create more reactants. Also show that if Q is smaller than K_p , the reaction will spontaneously create more products.

5. In our study of phase equilibrium we found that a substance with weaker intermolecular forces has a greater vapor pressure than a substance with strong intermolecular forces. This was explained using dynamic equilibrium arguments. Use thermodynamic equilibrium arguments involving ΔH , ΔS , and ΔG to explain why a substance with weaker intermolecular forces has a greater vapor pressure than one with stronger intermolecular forces.